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## Doctor's Dissertation

The Effect of Chain Growth  
Retardation in the Graft Polymerization  
of Styrene onto Cellulose Acetate

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THE EFFECT OF CHAIN GROWTH  
RETARDATION IN THE GRAFT POLYMERIZATION  
OF STYRENE ONTO CELLULOSE ACETATE

A thesis submitted by

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## SUMMARY

Past researches on the heterogeneous gamma ray-induced graft polymerization of styrene onto cellulosic substrates indicate that transport phenomena have a pronounced effect on the grafting reaction. However, the effect of a retarding agent on the yield, chemical composition, molecular weight, and long-chain structure of graft polymers upon the effect of a retarding agent is unknown. Addition of a retarding agent should increase the ratio of the monomer diffusion rate to the rate of chain propagation. Since conditions can be easily chosen so that additions of a retarding agent have a negligible effect on the swollen state of the substrate, the role of monomer diffusion as a function of the degree of swelling of the substrate may then be clarified.

The primary objective of this thesis is to study the effect of nitrobenzene, a known retarding agent, upon the well-characterized graft polymerization of styrene from pyridine solution onto pyridine-swollen cellulose acetate film. Also, since this grafting system permits isolation of relatively pure graft polymers, a secondary goal is the investigation of the structure of the graft polymer.

Styrene was grafted from pyridine solution onto swollen cellulose acetate film by direct irradiation from  $\text{Co}^{60}$  gamma rays for a total dose of  $20 \times 10^6$  rads at a dose rate of  $0.44 \times 10^6$  rads per hour. Small amounts of nitrobenzene were added to most of the styrene-pyridine solutions. Sequential extraction of the irradiated films with benzene and aqueous acetone selectively removed homopolystyrene and ungrafted cellulose acetate, respectively. The chemical compositions of the isolated graft polymers were determined by carbon-hydrogen analyses. After acid hydrolysis of the graft polymers, molecular weights of the polystyrene side chains were determined by osmometry. The polystyrene samples formed in the absence of nitrobenzene all contained appreciable portions of insoluble material.

Molecular weights of the soluble portions of these samples were determined after separation by centrifugation. Some polystyrene samples were further characterized by intrinsic viscosity measurements.

The following conclusions are based upon the quantities of grafted polystyrene and grafted cellulose acetate. In the absence of nitrobenzene, graft polymerization was limited by diffusion-controlled growth processes when styrene concentrations were 65, 70, and 75 mole % styrene. At styrene concentrations of 57.5 and 60%, when the substrate is highly swollen, the monomer transport rate is sufficiently rapid so that chain growth is reaction-controlled. In the presence of nitrobenzene, chain propagation is reaction-controlled at all styrene concentrations.

Number-average molecular weights of the polystyrene side chains, measured after removal of the cellulose backbone, were always higher than those of the corresponding homopolymers formed in solution. This observation indicates that chain termination is diffusion-controlled within the swollen film. Nitrobenzene additions reduced the molecular weight. However, the amount of nitrobenzene necessary for significant molecular weight reduction was apparently dependent upon the state of substrate swelling. At the lower degrees of substrate swelling, relatively large amounts of nitrobenzene were necessary for significant D.P. reduction. When the substrate was highly swollen, trace additions of nitrobenzene caused marked reductions in the D.P., while further additions had little effect.

Appreciable insoluble residues in the polystyrene formed in the absence of nitrobenzene is strong circumstantial evidence that the polymer contained appreciable portions of cross-linked gels. The amount of insoluble material increased with increasing molecular weight of the associated soluble polystyrene.

The cross-linking is believed to originate from coupling reactions between grafted polystyrene chains, which were initiated by radicals formed on the grafted side chain. Experimental evidence for branched polystyrene was obtained from the results of intrinsic viscosity measurements, which indicate that the polystyrene was branched.

Nitrobenzene prevented the formation of cross-linked gels in all cases. This compound adds to chain radicals, forming an adduct too unreactive for further monomer addition. Termination between this nitrobenzene adduct radical and the polystyrene radical chain end proceeds by disproportionation, and not by coupling of chain ends. Therefore, the probability of cross-linking in the presence of nitrobenzene is greatly diminished.

The number of polystyrene side chains per cellulose acetate chain was determined, and found to exhibit no observable trends with either the styrene-pyridine ratio or the nitrobenzene concentration. The values suggested that between two to four cellulose chains were connected to one polystyrene chain, and suggest that the samples may contain occluded ungrafted cellulose acetate that was not removed by the purification procedure.

## INTRODUCTION

A graft copolymer may be defined as a high polymer, composed of at least two polymeric sections of different composition, chemically linked together. In the context of this discussion, a cellulose graft copolymer consists of a polymerized vinyl monomer chemically attached to a cellulosic backbone.

In recent years, attempts to graft polymerize vinyl monomers onto cellulose have aroused considerable interest. Of the many reaction schemes used to form graft polymers, the most successful and popular ones attempt to initiate vinyl polymerization by homolytic degradation of the anhydroglucose unit. Some initiating systems used include high energy ionizing radiation (1), photosensitizing dyes in conjunction with ultraviolet light (2), ferrous ion-hydrogen peroxide (3), or ceric ion oxidants (4). Because of its relevance to the present discussion, only grafting induced by ionizing radiation will be considered further.

Despite the voluminous literature published on graft polymerization, relatively few studies concern the kinetics and mechanisms involved in formation of a graft polymer. Furthermore, studies reporting the molecular weight and molecular weight distribution of graft polymers are quite infrequent. This lack of fundamental knowledge is unfortunate, since detailed knowledge of the kinetic factors affecting yields, molecular weights, and molecular weight distributions can be of great value. Potential physical and end-use properties, such as solubilities in different solvents, mechanical, surface, and thermal properties, should be greatly dependent upon the composition and purity of the graft polymer, and upon the molecular weight and molecular weight distribution of the grafted side chains.



## COMPLICATIONS IN CHARACTERIZATION OF GRAFT POLYMERS

To a great extent, the lack of knowledge in the area of graft polymerization is attributable to the many formidable complications which are met with attempts to characterize a graft polymer. Some of these complications are described briefly below.

Firstly, the product resulting from a graft polymerization reaction is usually a mixture of the graft polymer, the unreacted substrate polymer, and the homopolymer formed from the monomer used in grafting. Solubility differences between the graft polymer and one of the homopolymers are frequently not large enough to permit their separation. Consequently, preparation of a graft polymer with any degree of purity is unusual.

Secondly, determination of the molecular weights of the grafted side chains require that the grafted side chain be separated from the backbone chain. This is sometimes difficult, especially when the host polymer has a carbon-carbon skeleton. In this regard, a cellulosic backbone offers particular advantage, since this skeleton can be readily hydrolyzed away.

Thirdly, most grafting reactions proceed by a free radical mechanism. The presence of small amounts of impurities can totally inhibit polymerization. Also, chain termination in a free radical polymerization frequently occurs by coupling of chain ends. Since, in principle, the host polymer may have more than one growing radical chain, formation of an insoluble cross-linked graft polymer is possible, and complicates the isolation and characterization of graft polymers.

Fourthly, most graft polymerization reactions are heterogeneous. Topochemical considerations, such as the degree of substrate swelling and its effect on transport phenomena, must be considered as well as factors affecting kinetics in

homogeneous solution. The complications due to the heterogeneous nature of the graft polymerization reaction are quite important, and are elaborated in succeeding sections.

## HETEROGENEOUS NATURE OF GRAFT POLYMERIZATION

### EFFECT OF SUBSTRATE SWELLING

Many studies have established the importance of the degree of swelling of the grafting substrate upon the amount of graft polymerization. It has generally been found that a highly swollen substrate is necessary to form large amounts of graft polymer.

Huang and Rapson (1) investigated the effect of swelling agents on the gamma ray-induced direct radiation grafting of styrene onto cellulose. Grafting occurred readily when cellulose was preswollen in polar swelling agents such as water, formamide, formic acid, or dimethylsulfoxide, then immersed in bulk styrene or styrene-solvent solutions, and irradiated. However, no apparent grafting took place when the cellulose was unconditioned.

Similar results were found by Kesting and Stannett (5), who grafted styrene from a styrene-dioxane-water solution onto preirradiated cotton. They found a marked increase in the amount of grafting by increasing the amount of water added either to the cotton before the irradiation, or to the monomer solution.

Arthur and Blouin (6) irradiated cotton cellulose with  $\text{Co}^{60}$  gamma rays and then grafted acrylonitrile after irradiation. Low yields of graft polymer were obtained when irradiated cottons were treated with pure acrylonitrile, 5% acrylonitrile in water, and 32% acrylonitrile in dimethylformamide. However, high yields of graft polymer were obtained in 32% acrylonitrile in concentrated zinc chloride solutions, which have a strong swelling effect on cellulose.

Stannett, Wellons, and Yasuda (7) grafted styrene onto cellulose acetate films by direct irradiation from  $\text{Co}^{60}$  gamma rays. The effect of substrate swelling was studied by diluting the styrene with pyridine or dimethylformamide, which were solvents for the cellulose acetate. With bulk styrene, no measurable grafting took place. Dilution of the monomer with the swelling solvent caused large amounts of grafting. With increasing monomer dilution, the yield of graft polymer increased to a maximum, after which further dilution reduced the amount of graft polymer.

#### CHARACTERISTICS OF POLYMERIZATION IN HETEROGENEOUS MEDIA

Free radical polymerization proceeds by a chain reaction involving three major steps: initiation, propagation, and termination. However, the heterogeneous nature of the reaction must necessarily modify the three-step polymerization process. The formation of a grafted chain involves the steps which are listed below:

1. Formation of free radicals. In this study, radical formation is considered to be induced by the action of ionizing radiation.
2. Transport of the monomer to the active site on the substrate surface.
3. Addition of the monomer to the active site.

The last two steps are repeated to form a long chain. In the absence of chain transfer reactions, or combination with mobile radical fragments, termination requires mutual interaction of chain ends. Termination can then be expressed as:

4. Transport of chain segments so that adjacent chain ends assume a favorable interaction, and
5. Coupling of the chain ends.

Steps 2 and 4 involve the diffusion of either the reactant monomer, macromolecular chain segments, or both. Steps 1, 3, and 5 involve a chemical reaction.

If reaction conditions are such that the rate of monomer transport is sufficiently rapid so that addition of monomer is controlled by the concentration of monomer and radicals, and by their mutual reactivities, then chain growth is said to be reaction-controlled. Termination by mutual interaction of chain ends can be controlled by either the concentration and reactivity of radical chain ends (reaction-controlled), or by the rate at which chain ends can assume a favorable interaction (diffusion-controlled). Under a given set of reaction conditions, the polymerization reaction falls into one of three model cases:

Case I. Both propagation and termination are controlled by the rate of reaction;

Case II. Chain propagation is reaction-controlled; termination is diffusion-controlled;

Case III. Both propagation and termination are diffusion-controlled.

The case of diffusion-controlled propagation and reaction-controlled termination is a physical impossibility, since reaction between two radicals is favored over reaction between monomer and radical.

#### Case I

Under conditions where polymerization is reaction-controlled, the rate of propagation,  $R_p$ , is proportional to the product of the radical concentration  $[RM\cdot]$ , and the monomer concentration,  $[M]$ . The propagation rate coefficient,  $k_p$ , expresses the mutual reactivity of monomer and radical. The radical concentration can be replaced by an expression involving the rate of initiation,  $R_i$ ,

and the termination rate constant,  $\underline{k_t}$ , to yield the following expression:

$$R_p = - \frac{d[M]}{dt} = k_p [RM\cdot] [M] = \frac{k_p R_i^{1/2} [M]}{(2 k_t)^{1/2}} \quad (1)$$

The degree of polymerization,  $\underline{P_n}$ , is the number of polymerized monomer units divided by the number of molecules, and is kinetically expressed by the ratio of the rate of propagation,  $\underline{R_p}$ , to the rate of termination,  $\underline{R_t}$ . If termination occurs exclusively by combination of chain ends:

$$P_n = \frac{R_p}{R_t} = \frac{k_p [M]}{(2 k_t)^{1/2} R_i^{1/2}} \quad (2)$$

This kinetic treatment is derived in Chapiro's text (8). A more detailed summary of the kinetics of free radical polymerization is presented in Appendix I, p. 61.

## Case II

In a reaction occurring within a gel phase, radical chain interaction is unlikely. The termination rate coefficient,  $\underline{k_t}$ , is considerably decreased since the coefficient reflects the probability that radical chain ends will juxtapose rather than reflect the mutual reactivities of the radical pair. Diffusion-controlled termination, commonly known as the "gel effect," is represented by a decreased termination rate coefficient, and causes an accelerated reaction rate and large increases in the molecular weight of the polymer chain. Diffusion-controlled termination is discussed in further depth in Appendix II, p. 67.

## Case III

Since formation of a polymer within the gel requires transport of monomer from the bulk liquid phase into the interior of the gel, propagation may likely be governed by the rate of monomer diffusion into the gel. The monomer concentration within the gel substrate will then vary with the distance into the substrate

as well as with time. The treatment of diffusion with accompanying chemical reaction is discussed at length in Crank's text (9). Beyond any unit area normal to the flow of monomer, the rate at which monomer is immobilized by polymerization,  $S$ , is equal to the monomer flux through this region,  $J$ , minus the rate of polymerization,  $R$ .

$$\frac{\partial[M]}{\partial t} = S = J - R \quad (3)$$

The flux,  $J$ , can be written in terms of Fickian diffusion, and the rate of polymerization,  $R$ , is expressed by Equation (1). Rewriting these terms leads to the expression for diffusion with accompanying pseudo-first-order reaction.

$$\frac{\partial[M]}{\partial t} = D \frac{\partial^2[M]}{\partial x^2} - \frac{k_p R_i^{1/2}}{(2 k_t)^{1/2}} [M] \quad (4)$$

Solution of this partial differential equation, which requires appropriate boundary conditions, expresses the monomer concentration as a function of time,  $t$ , and distance,  $x$ . The rate of polymerization, and degree of polymerization, at any distance within the substrate, can then be calculated by Equations (1) and (2).

#### EVIDENCE FOR DIFFUSION-CONTROLLED TERMINATION

Considerable evidence indicates that chain termination in radiation-induced graft polymerization is diffusion-controlled. This evidence is based on the considerable difference between the molecular weight of the grafted side chain and that of the homopolystyrene formed in the surrounding solution.

Huang, Immergut, and Rapson (10), in grafting styrene onto cellulose, found grafted side-chain molecular weights from 400,000 to 600,000, while the molecular weight of the corresponding homopolystyrene was approximately 25,000. Stannett,

Wellons, and Yasuda (7), who grafted styrene onto swollen cellulose acetate films, obtained side-chain molecular weights from 150,000 to 2,000,000; corresponding values for homopolystyrene produced in solution were 60,000-70,000. Huang (11) grafted styrene to rayon and obtained side-chain molecular weights of 400,000 to 1,000,000 compared to values of 30,000-50,000 for solution-produced homopolystyrene.

This difference between the molecular weights of the polymers formed within a solid substrate and those formed in the surrounding solution clearly illustrates the magnitude of the gel effect. The inability of polystyrene chain ends to become mutually accessible causes large increases in the chain length.

The magnitude of the gel effect is further illustrated by results of experiments in which this effect is reduced. Stannett, Wellons, and Yasuda (7) produced polystyrene - cellulose acetate graft polymers in homogeneous solution and compared the molecular weight of the grafted side chains with that of the polystyrene homopolymer. The comparison was quite close. Side-chain molecular weights ranged from 24,000 to 39,000, while homopolymer molecular weights were 19,000 to 35,000. In homogeneous solution, interaction between chain ends is more likely, and the gel effect is reduced.

The reduction of the gel effect has also been accomplished by addition of chain transfer agents to graft polymerization systems. In the presence of a chain transfer agent, termination of the growing chain radical occurs by transfer of the radical to an intervening molecule, called the chain transfer agent. Since the transfer agent is usually a mobile small molecule, chain termination within the substrate is less likely to be diffusion-controlled.

These effects are found in the results of Hayakawa, Kawase, and Matsuda (12). These workers polymerized styrene onto cellulose acetate in the presence of solvents with varying chain-transferring ability. When benzene and toluene, which are not strongly chain-transferring (13), were replaced by ethylbenzene and isopropyl-benzene, which have more pronounced chain-transferring properties (13), the amount and molecular weight of grafted polystyrene was markedly reduced.

Similar results were found by Huang (11), who added small amounts of strongly chain-transferring carbon tetrachloride (14) to the styrene - rayon system. Although complicated by some secondary radiation phenomena, marked losses in the amount and molecular weight of the grafted polystyrene were found.

#### EVIDENCE FOR DIFFUSION-CONTROLLED GROWTH

Although chain growth is less likely to be diffusion-controlled than is chain termination, effects of diffusion-controlled propagation are found in some previous work.

One of the earliest indications that chain growth was diffusion-controlled was the inability of earlier researchers to graft large numbers of polystyrene chains to cellulose. Huang (15) grafted one side branch per 2000-10,000 glucose units by direct irradiation onto water-swollen cotton. Kobayashi (16), using the pre-irradiation technique, estimated one polystyrene per 8000 glucose units. Kraessig (17) reports work in which one polystyrene branch was distributed from between 2500 and 8000 glucose units.

With all these studies, no attempts were made to remove unreacted cellulose. The extremely low degree of polystyrene substitution indicates that a considerable portion of the cellulosic substrate remains ungrafted. Since these samples were water-swollen, inaccessibility of potential grafting sites due to insufficient



swelling only partially explains the low frequency of grafting. Slow monomer diffusion into potentially-available grafting sites is another reasonable explanation.

Stannett's detailed study (7) of the styrene-cellulose acetate grafting system lists the amount of original substrate remaining ungrafted. Even when films were highly swollen in pyridine solvent during reaction, approximately 70% of the acetate was ungrafted. While inconclusive in itself, the large amount of ungrafted substrate suggests that growth of the grafted side chain is governed by a slow rate of monomer transport.

Schindler, Wellons, and Stannett (18) measured the molecular weight distribution of the grafted polystyrene side chains resulting from the direct irradiation of a styrene-pyridine-cellulose acetate mixture. The calculated average values were  $\frac{M_w}{M_n} = 8.3 \times 10^5$  and  $\frac{M_n}{M_w} = 9.0 \times 10^4$ ; the resulting weight to number average ratio ( $\frac{M_w}{M_n}$ ) was 9.2. This distribution is quite broad. Since the chain length in a diffusion-controlled polymerization is dependent upon the distance of the growth site from the solid-liquid interface, the unusually broad spectrum of chain lengths suggests a diffusion-controlled growth process.

Matsuo, Iimo, and Kondo (19) grafted styrene onto polypropylene film. Using a microinterferometric technique which permitted direct observation of the change in refractive index across the cross section of the irradiated films, they measured the transverse distribution of graft polymer within the film. At low monomer concentrations, the concentration of polystyrene decreased continuously from the outside of the film into the interior. This behavior indicated that the rate of reaction exceeded the rate of reactant transport into the gel.

At higher concentrations, anomalous behavior was observed. The polystyrene concentration increased from the outside of the film to a maximum within the film interior. After this maximum, the concentration decreased sharply to a minimum at the center of the film. The observed maximum resulted from a localized gel effect which produced an accelerated reaction rate in the region of the maximum.

## OBJECTIVES

Much work has been done to clarify the phenomena involved in formation of a graft polymer, but the effect of a retarding agent in a graft polymerization system has not been investigated. The dependence of the yield, chemical composition, molecular weight, and long-chain structure of graft polymers upon the effect of a retarding agent is unknown. Addition of a retarding agent reduces the rate of chain growth, and thereby increases the ratio of monomer diffusion rate to reaction rate. Since conditions can be easily chosen so that addition of a retarding agent has a negligible effect on the swollen state of the substrate, the role of diffusion as a function of changes in the degree of substrate swelling may be clarified.

The primary objective of this thesis is to study the effect of a retarding agent upon a well-characterized graft polymerization system. Also, since such a study requires isolation of relatively pure graft polymers, a secondary goal is the investigation of the structure of the graft polymers produced.

## SELECTION OF SYSTEM

Of the many possible graft polymerization systems, the styrene - pyridine - cellulose acetate system employed by Stannett and co-workers (7,18,20,21) offers the most advantages. These workers have thoroughly characterized this system, and variations in the yield of graft polymer, length of side chains, and efficiency of the substrate toward grafting were studied as a function of the radiation dose, dose rate, substrate swelling, and change of swelling medium. Also, the molecular weight distribution of a graft polymer sample was determined, and the role of concurrent cellulose acetate degradation during radiation grafting was investigated. This extensive background work makes this system particularly desirable for further study.

Most importantly, the styrene - cellulose acetate graft polymers were found to be particularly amenable to simple separation from the corresponding homopolymers. Stannett (7,20) found that benzene extraction of the irradiated products specifically removed homopolystyrene, and that subsequent extraction with aqueous acetone specifically removed unreacted cellulose acetate. The purity of the resulting graft polymer was checked by dissolution of the graft polymer in dimethylformamide and precipitation in benzene, followed by precipitation in aqueous acetone. Virtually complete extraction was claimed with every sample examined.

## RADIATION CHARACTERISTICS

The radiation characteristics of the styrene - pyridine - cellulose acetate system are particularly advantageous. In graft polymerization induced by direct irradiation, the substrate polymer, rather than the monomer or solvent, should act as the chief source of initiating radicals. In this manner, homopolymer

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formation initiated by decomposition of the monomer or solvent is minimized. Therefore, the host polymer should be more labile to radiation degradation than the monomer or solvent. In this regard, styrene and pyridine are remarkably inert to the effects of gamma radiation. However, cellulose acetate is degraded by gamma rays.

Styrene is among the most radiation-inert of the common vinyl monomers. Table I, abstracted from data published in Chapiro's text (8) lists approximate free radical yields of some vinyl monomers. The resistance of styrene to gamma radiation stems from its highly conjugated structure, which can absorb large amounts of radiation without decomposition.

TABLE I  
FREE RADICAL YIELDS OF SOME VINYL MONOMERS

Monomer	$\frac{G_R}{\text{radicals per 100 ev.}}$
Styrene	0.69
Acrylonitrile	2.8-5.6
Ethylene	4.4
Methyl methacrylate	11.5
Vinyl acetate	12
Methyl acrylate	15

The radiation resistance of pyridine was discovered by Stannett, et al. (7), who studied the polymerization kinetics of homogeneous styrene - pyridine mixtures. Pyridine exhibited a free radical yield that was lower than, or approximately equal to, the free radical yield of styrene.

Cellulose acetate is degraded by the action of gamma rays. Wellons and Stannett (21) irradiated cellulose acetate, both in solution and as a film, at

25°C. and measured the degradation by changes in intrinsic viscosity. The calculated number of chain cleavages per radiation dose is taken from Stannett's data and is shown in Table II. The cellulose acetate is extensively degraded as a dry film, or when dissolved in a solvent which is labile to gamma radiation. However, when dissolved in aromatic solvents, degradation is slight. These aromatic compounds act as efficient radiation absorbents, and exert a considerable protective influence upon the cellulose acetate.

TABLE II

RADIATION DEGRADATION OF CELLULOSE ACETATE

Solvent	G (cleavages)
None (dry film)	5.24
Dimethylformamide (DMF)	2.28
Pyridine	1.45
Pyridine - toluene (70:30)	0.77
Pyridine - $\alpha$ -methyl styrene (70:30)	0.49
Pyridine - $\alpha$ -methyl styrene (50:50)	0.19
Pyridine - $\alpha$ -methyl styrene (10:90)	0.24 (swollen film)

In these degradation studies,  $\alpha$ -methyl styrene replaced styrene to simulate conditions used in graft polymerization.  $\alpha$ -Methyl styrene cannot propagate by free radical polymerization because of steric hindrance; however, it has a radical affinity close to styrene itself. Leavitt, Stannett, and Szwarc (22) found that the rates of addition of methyl and polystyryl radicals to  $\alpha$ -methyl styrene are, respectively, 1.2 and 1.4 times those found with styrene. The results of Table II show that  $\alpha$ -methyl styrene, and by inference, styrene, reduce the number of chain scissions of cellulose acetate. Wellons and Stannett (21) have postulated that the protective effect of these monomers is their ability to add to chain radicals

formed from the elimination of atoms or side groups from the backbone cellulose structure. In the absence of monomer, such chain radicals might disproportionate, eventually causing chain cleavage. In the presence of a monomer capable of propagation, such as styrene, monomer addition with subsequent graft polymerization occurs.

#### POLYMERIZATION CHARACTERISTICS

The free radical polymerization has been exhaustively studied, and good reviews are found in texts by Flory (23) and Chapiro (8). In the bulk polymerization of styrene, termination by chain coupling predominates (24). Chain transfer with monomer, which involves transfer of the radical center from the polystyryl radical to the monomer, is improbable. At 60°C. the chain transfer constant, which is the probability that the chain radical will transfer the radical to a monomer rather than adding monomer, is  $0.6 \times 10^{-4}$ , which is a low value.

Chain transfer properties of pyridine are unknown. However, most good chain transfer agents possess an easily abstractable hydrogen atom, a halogen atom, or possibly some labile group. The highly conjugated structure of pyridine makes strong chain-transferring properties unlikely.

The solution properties of styrene and pyridine offer further advantages. Both styrene and pyridine are solvents for polystyrene. Consequently, precipitation of growing polystyrene with its incipient gel effect need not be considered. Pyridine is a solvent for cellulose acetate, while styrene is not. Therefore, dilution of styrene with pyridine increases the swollen state of the cellulose acetate substrate.

## RETARDATION PHENOMENA

Nitrobenzene is a suitable retarding agent in the free radical polymerization of styrene. Small amounts of this compound depress the rate of styrene polymerization without totally suppressing polymerization.

Inhibition and retardation phenomena are an important consideration in this study. Substances which may prevent chain growth are often classified on the basis of their effectiveness. Inhibitors effectively stop the growth of every chain until the inhibition agent is consumed. Retarders, which are less effective than inhibitors, merely slow, rather than stop, the polymerization process.

The apparent differences between the two classes upon the thermal polymerization of styrene are shown in Fig. 1, which was abstracted from the original work of Schulz (25) by Flory (23). Curve I represents the thermally initiated polymerization of pure styrene at 100°C. In the presence of 0.1% benzoquinone (Curve II), a typical inhibitor, an inhibition period is followed by polymerization at essentially the same rate as in pure styrene. No inhibition period is observed in the presence of 0.5% nitrobenzene (Curve III), which is a good example of a retarder. Instead, the reaction rate is reduced to approximately one-third its normal rate throughout the entire period of measurement. Nitrosobenzene (Curve IV) is an inhibitor. However, after the induction period, the polymerization is still slower than normal. Apparently, the reaction products of the initial inhibition reaction act as retarders.

Although this classification is convenient, it is emphasized that differences between inhibitors and retarders are one of degree rather than mechanism. For example, a large quantity of retarder may bring about a complete stop to polymerization. Also, sensitive measurement techniques may detect polymerization proceeding during an apparent induction period.



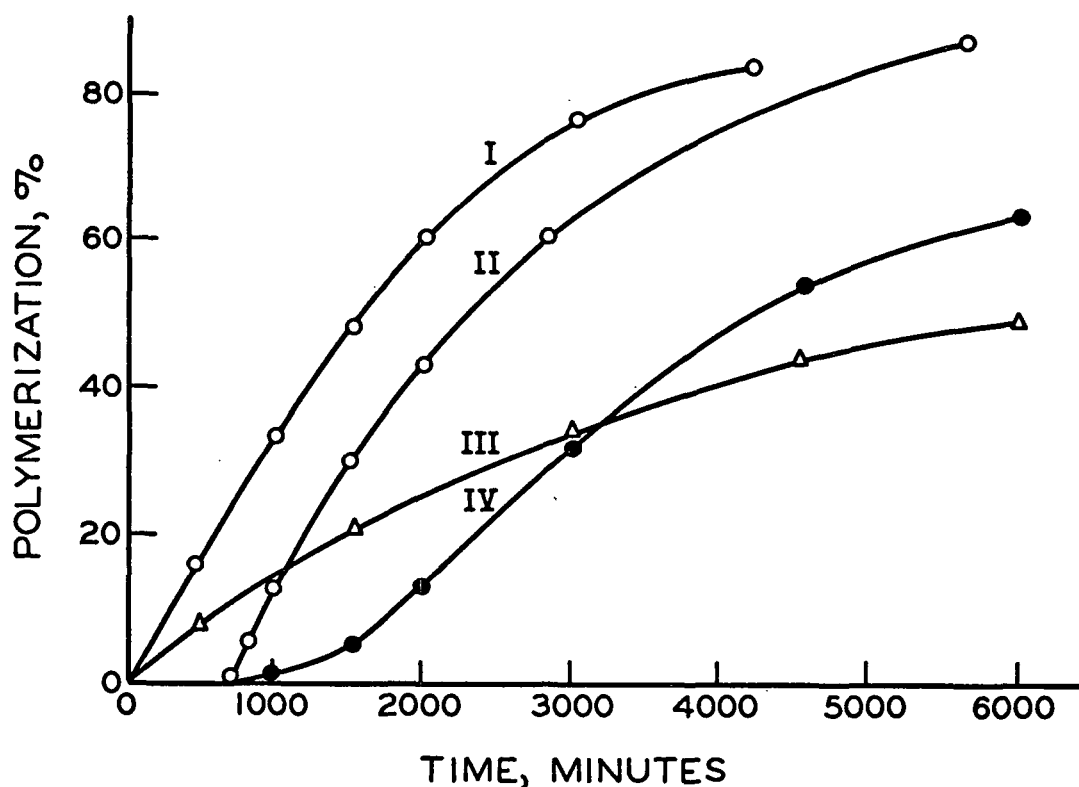
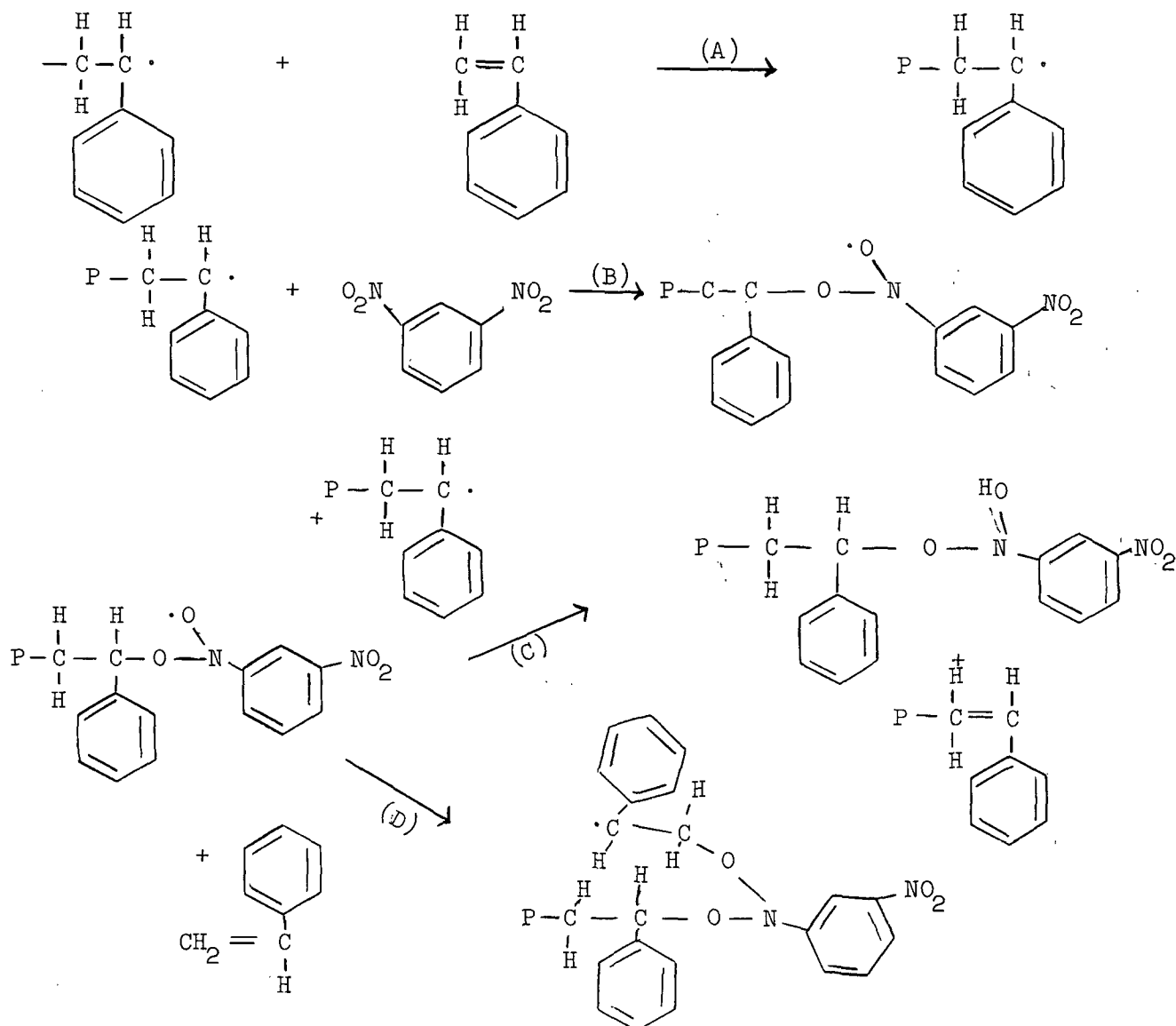


Figure 1. A Comparison of the Effects of 0.1% of Benzoquinone (Curve II), 0.5% of Nitrobenzene (Curve III), and 0.2% of Nitrosobenzene (Curve IV) on the Thermal Polymerization of Styrene at 100°C. Curve I Represents the Polymerization of Pure Styrene (Results of Schulz)\*

The mechanism of inhibition and retardation has been studied by Bevington and Ghanem (26) in the azobisisobutyronitrile-sensitized polymerization of styrene. Using isotopic tagging techniques, the mechanism of retardation of  $C^{14}$ -labeled m-dinitrobenzene, an analog of nitrobenzene, was studied. The proposed mechanism for the action of m-dinitrobenzene on the free radical polymerization of styrene is as follows:

\*Graph taken from Flory, P. J. (23), p. 162.



Step A illustrates the growth reaction between styrene and the polystyryl radical. In Step B, the growing polystyryl radical reacts with the aromatic nitro compound to form an alkoxy amine radical. Evidence of the linkage of polystyrene to the nitro group is based on the results of the reaction of the labeled dinitrobenzene - polystyrene adduct with trifluoroacetic anhydride, which lowered the radioactive count of the polymer. Since treatment with trifluoroacetic anhydride would not cleave carbon-carbon bonds, the addition must have occurred to the nitro group.

In Step C, the alkoxy amine radical disproportionates with the polystyryl radical to form an unsaturated polystyrene and the hydroxy-alkoxy amine. At high dinitrobenzene concentrations, mutual termination is suppressed, suggesting disproportionation rather than coupling. If Step C predominates over Step D then one initiator fragment and one-half of a retarder molecule would be combined to each polymer molecule. To a great degree, results substantiated this prediction. Reaction D was concluded to occur to a minor extent, however, since slightly more than one-half of a retarder molecule was bound to each polymer molecule. The low probability of Reaction D explains the retarding effect of aromatic nitro compounds.

## EXPERIMENTAL TECHNIQUES

### SOLVENT PURIFICATION

Styrene monomer was freed of inhibitors and trace aldehyde by the method of Blout and Mark (27). Reagent-grade styrene was vigorously shaken in 5% sodium hydroxide solution, then washed with distilled water until the aqueous extract was neutral, dried over anhydrous calcium chloride overnight, and then vacuum distilled. The purified styrene was stored in a dry ice chest prior to use, usually within 24 hours of the radiation run.

Pyridine was purified by distillation over barium oxide (28). Reagent-grade nitrobenzene was slowly distilled under vacuum on a spinning band column, a middle fraction being kept. Acetone was refluxed for 48 hours over potassium permanganate, distilled and dried over potassium carbonate (29). All other solvents employed were reagent grade and were used without further purification.

### FILM CASTING PROCEDURES

Cellulose acetate (D.S. = 1.70), kindly provided by Eastman Kodak, was dissolved in pyridine and filtered through a 1.5 micron "Millipore OH" membrane to remove insoluble haze. The clarified solution was then concentrated to form a viscous sirup. Films were cast on clean plate glass with a 0.014-inch clearance Bird bar, peeled from the glass plates, and then dried in vacuo at 60°C. for at least two days. Film thickness was 0.0020-0.0025 inch.

When immersed in styrene - pyridine solutions, the degree of swelling of the films was dependent upon the relative amount of pyridine in the monomer solution. In this study, the molar percentage of styrene in the monomer solution was varied from 57.5 mole % styrene to 75 mole % styrene. When the styrene

concentration was 57.5% styrene, the films were highly swollen and quite plastic. However, when the styrene concentration was 75% styrene, the films were quite brittle.

#### IRRADIATION CONDITIONS

Cellulose acetate films were cut into strips, approximately 7 inches by 1 inch, and wrapped in glass wool to prevent the faces of the film strips from coming in contact. The samples were then inserted into reaction tubes containing the monomer-solvent solution. The reaction tubes consisted of ten-inch test tubes stoppered with 24/40 ground glass joints and a stopcock. Dissolved oxygen gas was removed from the reaction mixtures by evacuation on an aspirator line followed by vacuum relief with nitrogen. All samples were given at least three degassing cycles.

The irradiations were performed using the  $\text{Co}^{60}$  facilities at the Cook Technological Center of the Cook Electric Company at Morton Grove, Ill. The sectional view of this source is shown in Fig. 2. The dose rate was  $0.422 \times 10^6$  rads/hr. Total dose was  $20 \times 10^6$  rads.

The reaction tubes were housed in a specially-constructed 15-inch diameter, 8-1/2-inch high, aluminum holding fixture which rotated within the annular source at 33 r.p.m. A picture of the holding fixture with reaction tubes is shown in Fig. 3.

#### ISOLATION OF GRAFT POLYMERS

The irradiated films were extracted for two days with hot benzene to remove homopolystyrene. The efficacy of this procedure was checked by measurement of the infrared spectra of the freeze-dried extract. In all cases, the infrared

spectra of the extracted homopolystyrene was identical to that of a known sample of polystyrene (Koppers, extra fine). If cellulose acetate were present in the extracted sample, a noticeable shift in the band intensity of the carbonyl stretching frequency at  $1740\text{ cm.}^{-1}$  would have been observed. Since no evidence was found for the presence of cellulose acetate, it was concluded that benzene extraction of the irradiated films specifically removed homopolystyrene.

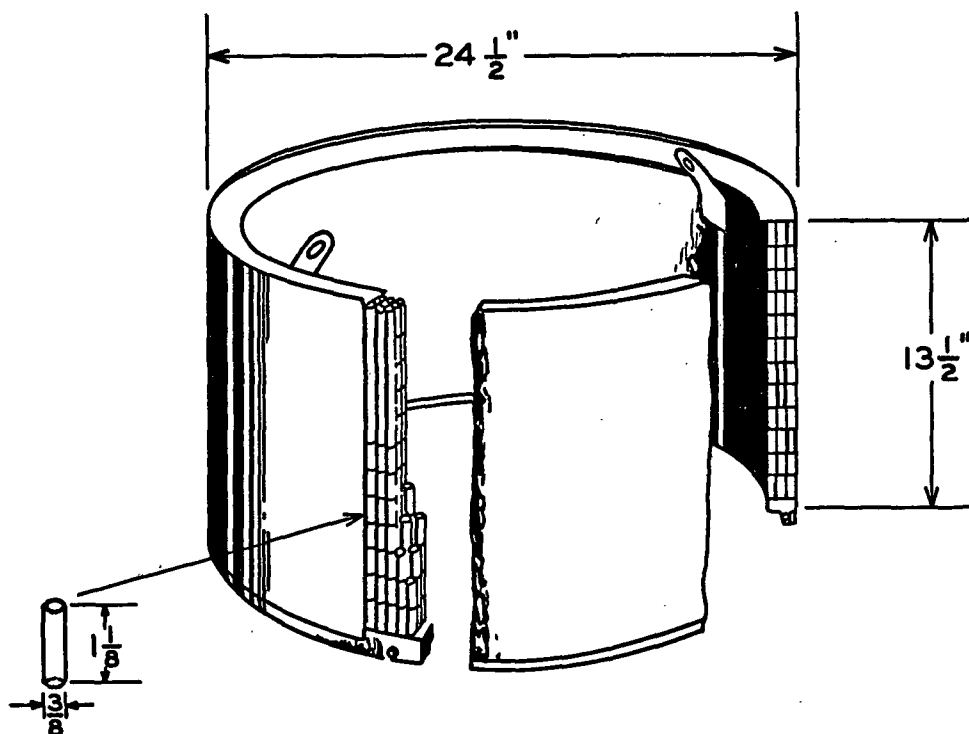


Figure 2. Sectional View of Cobalt<sup>60</sup> Source\*

After drying at  $60^{\circ}\text{C.}$  in vacuo, the films were extracted for two days in acetone - water solutions (55:45). Infrared spectra of some of the dried aqueous acetone extracts were identical to the spectra of the original cellulose acetate. Since aromatic materials could not be detected, it was concluded that acetone - water extraction of the irradiated films specifically removed unreacted cellulose acetate.

\*Picture taken from pamphlet by Cook Electric Co. entitled "Nuclear science capabilities."

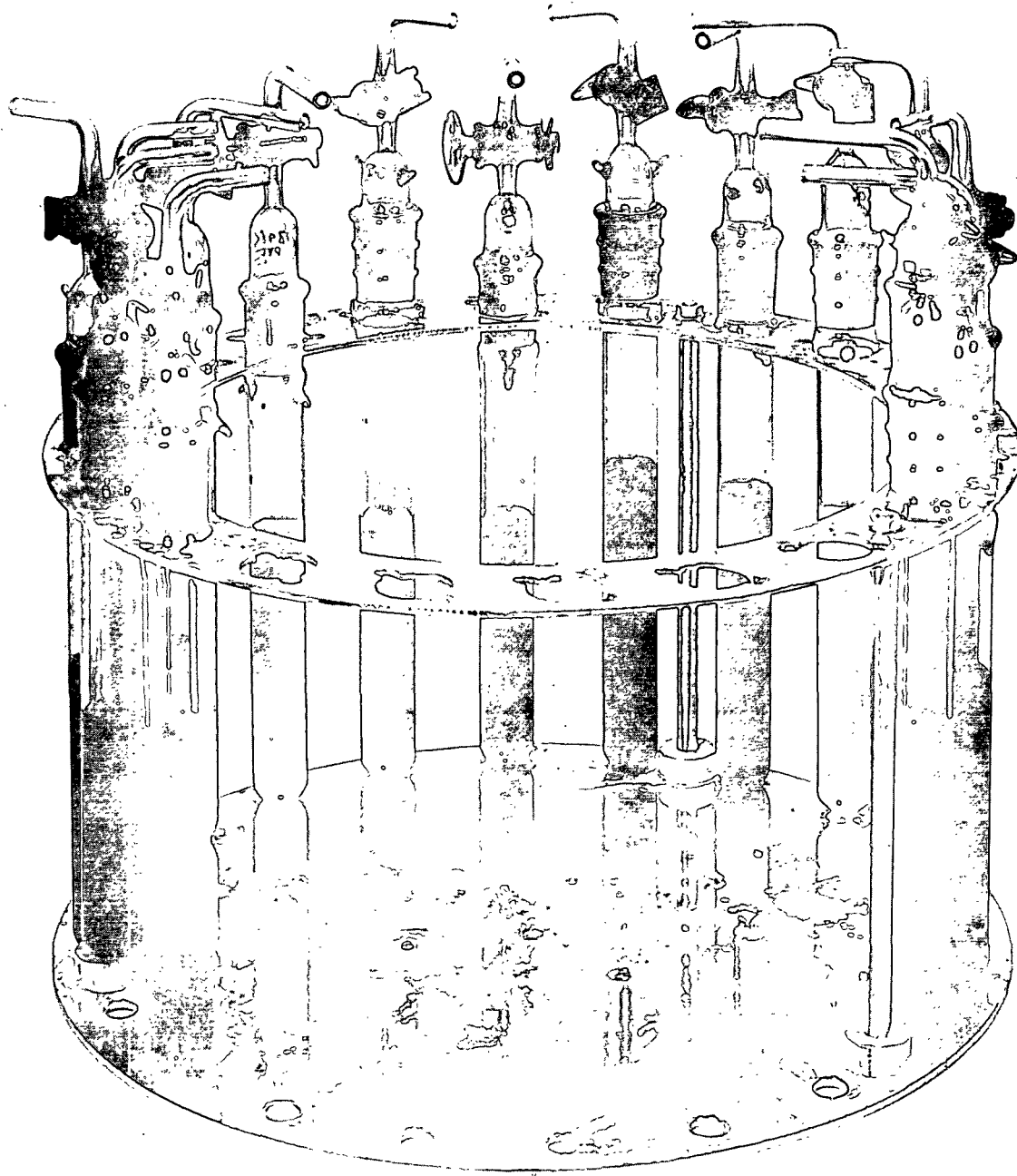


Figure 3. Aluminum Holding Fixture

Separation of graft polymers from the undesired homopolymers was achieved by using the sequential extraction procedure first described by Stannett, et al. (20). Hot benzene was used to extract homopolystyrene, followed by aqueous acetone extraction of the unreacted cellulose acetate. Each sample was given two such extraction cycles. The amounts of material removed on the second extraction cycle were apparently insignificant. The second benzene extract produced no apparent precipitate upon pouring into methanol; no precipitate formed from evaporation of the acetone from the second aqueous acetone extract.

#### COMPOSITION OF THE GRAFT POLYMERS

Carbon-hydrogen analyses of the isolated graft polymer samples were used to determine the relative amounts of polystyrene and cellulose acetate. Polystyrene contains 92.3% carbon; cellulose acetate (31.1% acetyl) contains 48.3% carbon. Therefore, the difference in carbon content between polystyrene and cellulose acetate provides a sensitive means for determining the composition of a graft polymer sample.

The graft polymer samples were ground in a micro-ball mill for one minute and were submitted to Geller Microanalytical Laboratories at Charleston, West Virginia for carbon - hydrogen analyses. For reference purposes, a sample of cellulose acetate, obtained by aqueous acetone extraction of an irradiated film, and a sample of polystyrene, obtained by acid hydrolysis of a graft polymer sample, were submitted to determine the carbon contents of cellulose acetate and polystyrene, respectively. Compositions were based on these experimentally determined carbon contents which were 91.5% and 47.2% for the polystyrene and cellulose acetate, respectively.



Also, carbon - hydrogen - nitrogen analyses were run on two hydrolyzed polystyrene samples to determine the amount of any bound nitrogen.

#### HYDROLYSIS OF THE GRAFT POLYMERS

Isolated graft polymers were hydrolyzed in sulfuric acid to liberate the polystyrene side chains. Approximately 0.2 gram of graft polymer was pulverized in a micro-ball mill for one minute, and then swollen in 72% sulfuric acid for 24 hours. After dilution to 3% sulfuric acid, the samples were heated for 1-1/2 hours at 115°C. in an autoclave. The samples were then neutralized with excess sodium acetate, filtered, thoroughly washed with distilled water, and dried in vacuo at 60°C. for at least 24 hours.

#### OSMOMETRY

Number average molecular weights of hydrolyzed graft polymer solutions in toluene were determined using the Mechrolab model 501 high-speed membrane osmometer (30). Solvent-resistant type 07 cellulose membranes (Schleicher & Scheull, Inc.) were used. With this instrument in proper running order, the equilibrium osmotic pressure across the membrane separating solution from solvent is rapidly established. By measuring osmotic heads at a number of solution concentrations, molecular weights are easily calculated using the well-known van't Hoff equation (23)

$$\frac{\pi}{c} = \frac{RT}{M_n} \quad (5)$$

where

$\pi$  = osmotic pressure in cm. of solvent

$\underline{c}$  = concentration in g./liter

$\underline{R}$  = gas constant

$\underline{T}$  = absolute temperature

$\underline{M}_n$  = number average molecular weight.

The extrapolated value of  $(\pi/\underline{c})$  at zero concentration is used for molecular weight calculations. A least squares fit was used to obtain this extrapolated value.

All of the polystyrene samples which were grafted in the absence of nitrobenzene contained appreciable fractions of toluene-insoluble material. Molecular weights of the soluble portions of these samples were determined after centrifugation. The fraction of insoluble material was determined by weighing the solid residue remaining after a second toluene extraction of the insoluble gel.

Solution concentrations were determined by either of two methods, which agreed to within 2%. Some concentrations were determined by preparing a known volume of solution with a measured weight of sample. This method was replaced by the more accurate technique of evaporating a 1.0-ml. aliquot of filtered solution at 104°C., which is above the second-order transition of polystyrene, in vacuo for twenty-four hours.

#### VISCOMETRY

Viscometry measurements of some polystyrene side-chain samples in toluene were conducted in a number 25 Cannon Ubbelohde semimicro dilution viscometer at  $30.00 \pm 0.03^\circ\text{C.}$ , with which shear rate and kinetic energy corrections are negligible. All solutions were filtered at least twice through a 0.8 micron Millipore membrane before determining viscosities.

Intrinsic viscosities,  $[\eta]$ , were determined according to the following equation (23)

$$\frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c \quad (6)$$

by extrapolating the curve of  $\eta_{sp}/c$  vs.  $c$  to infinite dilution.

## RESULTS AND DISCUSSION

### AMOUNT OF GRAFT POLYMER

Table III lists the percent yield of the isolated graft polymers, the weight percent of grafted polystyrene, and weight percent of graft cellulose acetate, all based on the weight of the original film. These values are presented with the corresponding styrene - pyridine mole ratio, and percent nitrobenzene. Replicate runs are indicated by (A) and (B) notations. The percentages of grafted polystyrene and grafted cellulose acetate were calculated from the composition of the isolated graft polymer, which was obtained from results of carbon-hydrogen analyses. These results are also listed in Table III, showing the measured percent carbon and the calculated percent polystyrene in the graft polymer. From knowledge of the yield and composition of the graft polymer, the weight percentages of polystyrene and cellulose acetate are calculated.

The difficulty in obtaining reproducible results is immediately evident, for the experimentally determined yields and compositions of the graft polymers on duplicate samples are usually quite scattered. Consequently, considerable scatter is found in the calculated amounts of grafted polystyrene and cellulose acetate.

Despite this, definite trends can be observed with respect to the effect of the styrene - pyridine ratio and the nitrobenzene concentration. Figures 4 and 5, which plot the percent grafted polystyrene and percent grafted cellulose acetate, respectively, as a function of the styrene concentration, graphically illustrate these trends. On both of these graphs, average values of the duplicate samples are used.

TABLE III

## WEIGHTS AND COMPOSITIONS OF GRAFT POLYMERS

Mole Ratio Styrene - Pyridine	Nitro- benzene, %	Carbon, %	Polystyrene incGraft Polymer, % <sup>a</sup>	Weight % Yield of Graft Polymer	Weight % Grafted Polystyrene	Weight % Grafted Cellulose Acetate
75/25	--	72.83	57.87	31.3	18.1	12.2
75/25	0.1	71.76	55.46	71.5	30.0	31.9
75/25	0.5	65.22	40.69	55.1	22.4	32.7
70/30 (A) <sup>b</sup>	--	73.55	59.50	46.6	27.7	18.9
70/30 (B)	--	74.46	61.56	37.0	22.8	14.2
70/30 (A) <sup>b</sup>	0.1	71.72	55.37	71.8	39.7	37.1
70/30 (B)	0.1	70.59	52.82	70.2	37.1	33.1
70/30 (A)	0.5	65.09	40.41	56.2	22.7	33.5
70/30 (B)	0.5	65.14	40.52	54.2	21.9	32.3
65/35 (A)	--	73.25	58.83	49.3	29.0	20.3
65/35 (B)	--	74.46	61.56	84.2	51.8	32.4
65/35 (A)	--	73.97	60.45	24.8	15.0	9.8
65/35 (B)	--	77.20	67.74	40.1	27.2	12.9
65/35 (A)	0.02	74.71	62.12	65.3	40.6	24.7
65/35 (B)	0.02	74.35	61.31	77.8	47.7	30.1
65/35 (A)	0.05	72.92	58.08	56.1	32.6	23.5
65/35 (B)	0.05	72.41	56.93	67.9	38.6	29.3
65/35 (A)	0.1	68.96	49.14	67.1	33.0	34.1
65/35 (B)	0.1	68.42	47.92	64.4	30.9	33.5
65/35 (A)	0.5	64.55	39.18	51.1	20.0	31.1
65/35 (B)	0.5	65.11	40.45	50.9	20.6	30.3
60/40 (A)	--	75.48	63.86	92.4	59.0	33.4
60/40 (B)	--	73.38	59.12	86.0	50.8	35.2
60/40 (A)	--	74.15	60.86	60.2	36.6	23.6
60/40 (B)	--	75.06	62.91	66.2	41.5	14.7
60/40 (A)	0.02	69.40	50.13	71.9	36.0	35.9
60/40 (B)	0.02	67.00	44.72	62.5	28.4	35.1
60/40 (A)	0.05	68.25	47.54	74.0	35.2	38.8
60/40 (B)	0.05	65.06	40.34	51.5	20.8	30.7
60/40	0.1	67.58	46.03	58.1	26.7	31.4
60/40	0.1	67.77	46.45	58.7	27.3	31.4
60/40 (A)	0.5	64.98	40.16	--	--	--
60/40 (B)	0.5	59.36	27.47	42.0	11.5	30.5
57.5/42.5	--	71.22	54.24	70.3	38.1	32.2
57.5/42.5 (A)	0.02	62.84	35.33	48.6	17.2	31.4
57.5/42.5 (B)	0.02	64.28	38.58	54.1	20.9	33.2
57.5/42.5 (A)	0.05	61.93	33.27	36.8	12.2	24.6
57.5/42.5 (B)	0.05	60.89	30.92	36.9	11.4	25.5

<sup>a</sup>Calculations based upon the following experimentally determined carbon contents:

Polystyrene - 91.49% carbon; cellulose acetate - 47.19% carbon.

<sup>b</sup>Nitrogen content of hydrolyzed polystyrene samples was 0.83% on two different samples.

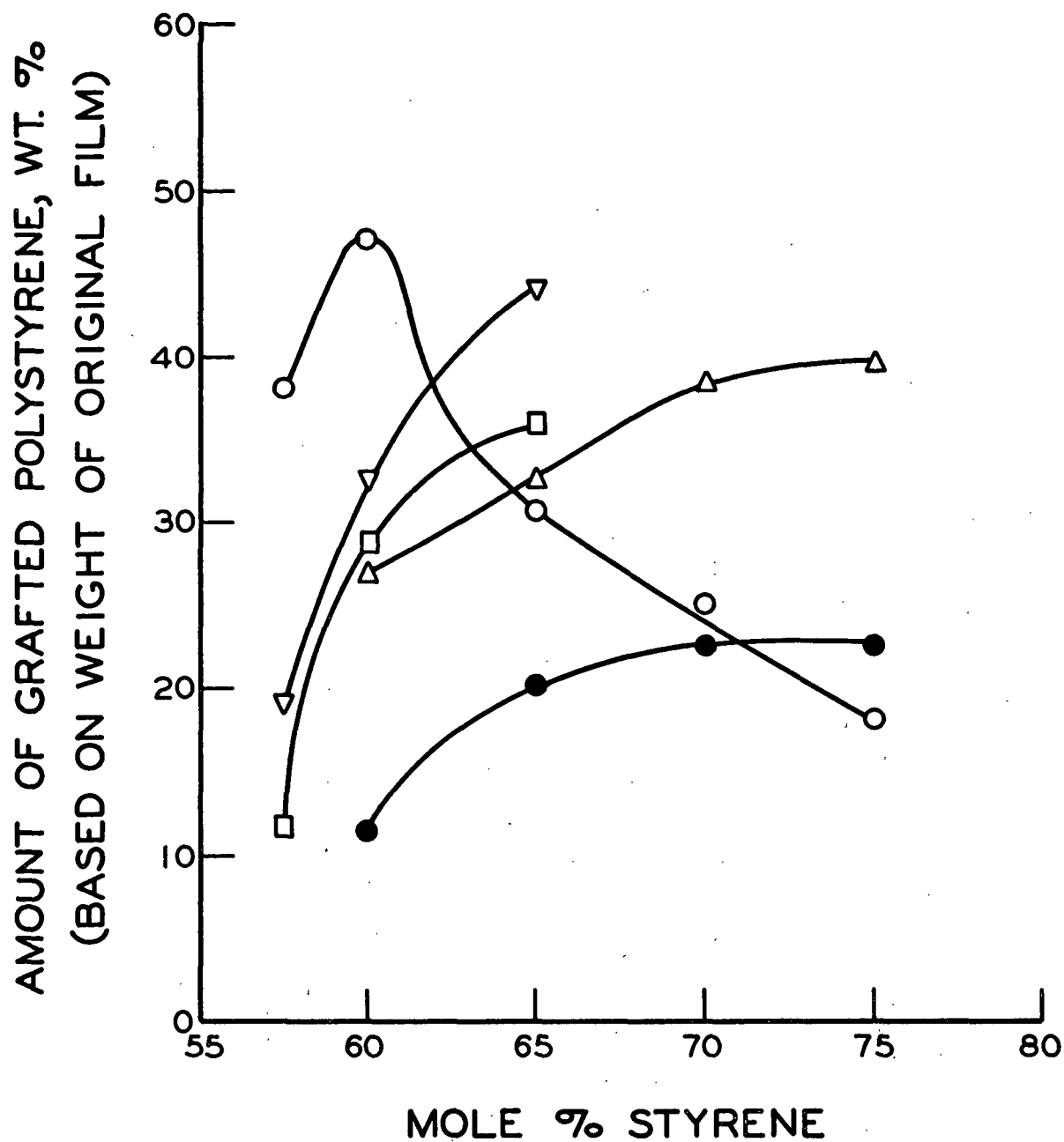


Figure 4. Amount of Grafted Polystyrene; ○ - no Nitrobenzene;  
▽ - 0.02% Nitrobenzene; □ - 0.05% Nitrobenzene;  
△ - 0.10% Nitrobenzene; ● - 0.50% Nitrobenzene

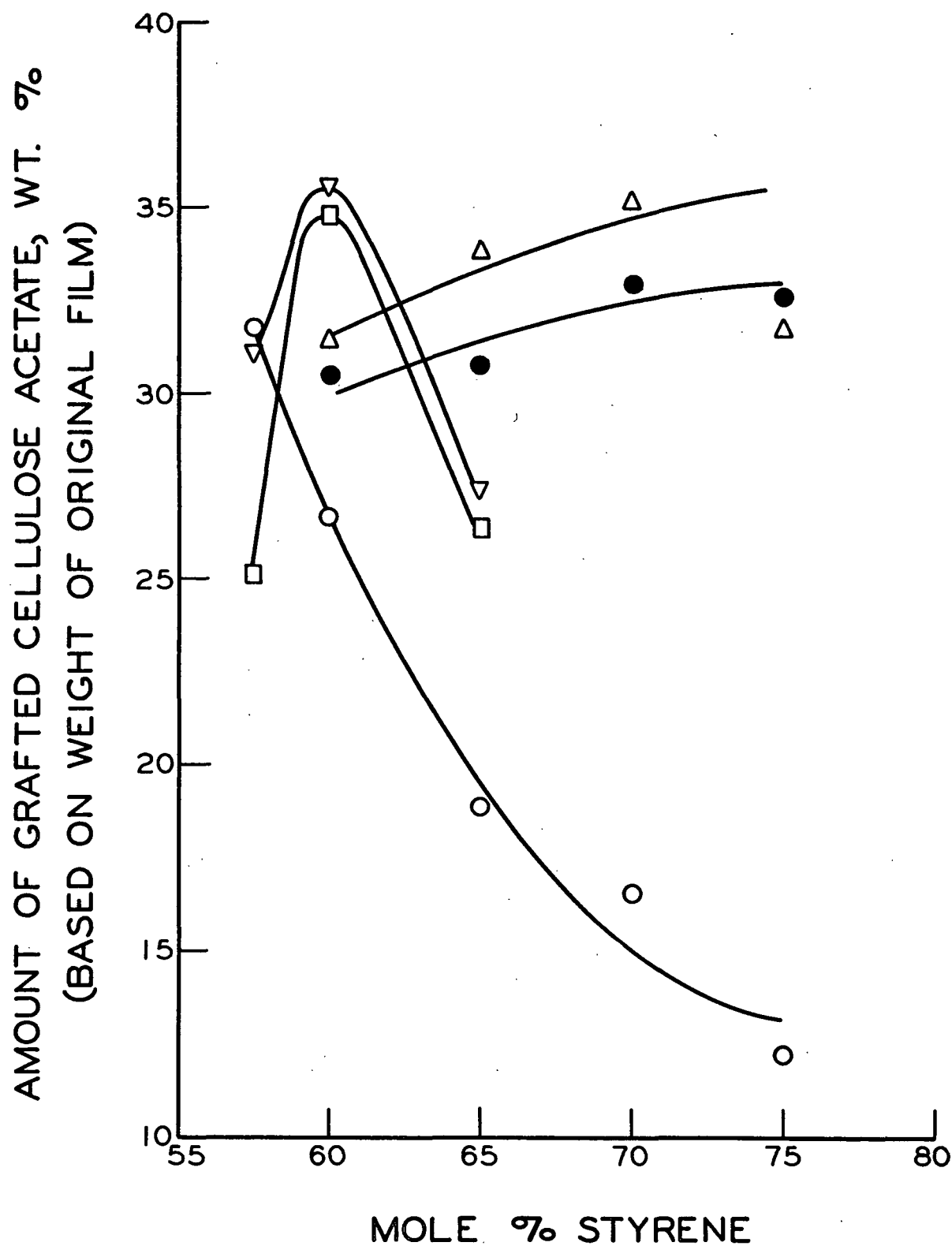


Figure 5. Amount of Grafted Cellulose Acetate; O - no Nitrobenzene; ▽ - 0.02% Nitrobenzene; □ - 0.05% Nitrobenzene; △ - 0.10% Nitrobenzene; ● - 0.50% Nitrobenzene

#### AMOUNT OF GRAFTED POLYSTYRENE

As shown in Fig. 4, in the absence of nitrobenzene, the amount of grafted polystyrene increases as the styrene concentration is increased from 57.5 to 60%, and then decreases from over 40 to 17% as the monomer concentration is increased from 60 to 75%. The increasing styrene concentration is accompanied by a noticeable decrease in the degree of swelling of the cellulose acetate substrate.

Additions of nitrobenzene to the styrene - pyridine solutions produced pronounced effects on the quantity of grafted polystyrene. Nitrobenzene additions cause smaller quantities of grafted polystyrene at the lower styrene concentrations, and larger quantities at the higher monomer concentrations. At any nitrobenzene concentration, the quantities of grafted polystyrene increase with increasing styrene concentration, and appear to be independent of the swollen state of the film. Larger amounts of nitrobenzene reduce the amount of polystyrene at any monomer concentration.

#### AMOUNT OF GRAFTED CELLULOSE ACETATE

In the absence of nitrobenzene, the weight percent of substrate in grafted form decreases as the styrene concentration increases. The decrease in the styrene concentration is accompanied by a reduction in the degree of substrate swelling. As shown in Fig. 5, the reduction is quite pronounced, decreasing from over 30% at a concentration of 57.5% to below 15% at a styrene concentration of 75%. At the higher monomer concentrations, when the cellulose acetate is not highly swollen, addition of nitrobenzene causes marked increases in the quantity of grafted cellulose acetate. Further monomer dilution with pyridine causes greater substrate swelling and the effects of nitrobenzene additions at the low styrene concentrations are not great. At the lowest styrene concentration,



nitrobenzene additions apparently reduce the weight of substrate in grafted form. The experimental scatter makes interpretation of the effect of increasing nitrobenzene concentration difficult, since the changes in the percentage of substrate grafting are not very large and are obscured by the experimental error.

## DISCUSSION

Physically-realistic models for diffusion-controlled and reaction-controlled propagation have previously been described by the kinetic equations on pages 9 and 10. These models form a reasonable basis for discussion of the effects of increased monomer concentration, increased degree of substrate swelling, or increased nitrobenzene concentration upon the amount of grafted polystyrene and grafted cellulose acetate. Table IV shows the expected effect of an increased monomer concentration, increased degree of substrate swelling, or increased nitrobenzene concentration upon the amount of grafted polystyrene and grafted cellulose acetate when propagation follows a diffusion-controlled model, and when propagation is apparently reaction-controlled. The application of these models to the experimental results is discussed in the following section.

### Diffusion-Controlled Growth

Under conditions where the chain propagation is diffusion-controlled, the rate of monomer transport is described by Equation (4)

$$\frac{\partial[M]}{\partial t} = D \frac{\partial^2[M]}{\partial x^2} - \frac{k_p R_i^{1/2}}{(2k_t)^{1/2}} [M].$$

When growth is diffusion-controlled, a reduction in the styrene concentration reduces the rate of reaction. An increased monomer flux might result from this reduced reaction rate. However, the reduced monomer concentration in the surrounding solution should reduce the concentration gradient ( $\partial[M]/\partial x$ ), which is

the driving force necessary for monomer diffusion. Consequently, the effect of a reduced monomer concentration, per se, is impossible to predict.

TABLE IV  
EXPECTED RESULTS

	Diffusion-Controlled Growth	Reaction-Controlled Growth
Higher styrene concentration	impossible to predict	increased amount of grafted polystyrene,  little effect on amount of grafted cellulose acetate
Increased degree of substrate swelling	increased amount of grafted polystyrene,  increased amount of grafted cellulose acetate	impossible to predict
Increased nitrobenzene concentration	increased amount of grafted polystyrene,  increased amount of grafted cellulose acetate	decreased amount of grafted polystyrene,  little effect on amount of grafted cellulose acetate

More important is the effect of the higher pyridine concentration resulting from the reduction of the styrene concentration. Larger percentages of pyridine in the surrounding solution cause the films to swell, and noticeably increase the plasticity of the films. Therefore, the diffusion coefficient and rate of monomer transport are increased. Increased amounts of grafted polystyrene and grafted cellulose acetate should result from the increased monomer transport rate.

Addition of nitrobenzene reduces the rate of reaction without significantly affecting the initial monomer concentration. Its effect is apparent as a reduction in the propagation rate constant,  $k_p$ . The reduced rate of reaction also lowers the rate of homopolymerization in the surrounding solution, and thereby increases the monomer concentration with time at the solid-liquid interface. Consequently,

a relatively larger concentration gradient between points within the film and the bulk monomer solution is maintained. Therefore, the overall monomer flux,  $\underline{J}$ , is increased. The reduced rate of reaction and larger concentration gradient cause an increase in the monomer transport rate. Increased amounts of grafted polystyrene and cellulose acetate are the expected result.

This model for diffusion-controlled growth is applicable to some of the reaction conditions employed in this study. The grafting reactions at concentrations of 65, 70, and 75% styrene without nitrobenzene follow the model for diffusion-controlled growth. In these three cases, further swelling induced by a greater pyridine concentration, or a reduced reaction rate by addition of nitrobenzene, cause larger quantities of grafted polystyrene and grafted cellulose acetate.

#### Reaction-Controlled Growth

When chain growth is not diffusion-controlled, the rate of chain growth is described by Equation (1) on page 9.

$$R = \frac{k_p R_i^{1/2} [M]}{(2k_t)^{1/2}}$$

Under these conditions, the reduction in the monomer concentration will lower the reaction rate, and thereby lower the amount of grafted polystyrene. However, the additional pyridine may swell the substrate so that previously inaccessible radical sites are capable of adding monomer. The increased number of sites would tend to increase the rate of reaction. Consequently, the effect of monomer dilution upon the rate of grafting cannot be predicted.

However, an observed decrease in amount of grafted polystyrene with an increased degree of swelling strongly suggests that growth is reaction-controlled. Such an observation indicates that any added accessible radical sites have an

insignificant effect on the rate of reaction, and that the lower monomer concentration reduced the rate of reaction.

The effect of nitrobenzene in the reaction-controlled system is predictable. Under similar conditions of substrate swelling, additions of nitrobenzene retard the rate of polymerization, lowering the quantity of grafted polystyrene. Since the swollen state is essentially unchanged, and since the monomer transport rate is sufficiently rapid, the percent of grafted cellulose acetate should be relatively unaffected by additions of nitrobenzene.

The criteria for observation of a reaction-controlled growth process can therefore be developed. A reduced quantity of grafted polystyrene upon reducing the monomer concentration, or upon the addition of nitrobenzene, demonstrates that chain growth is reaction-controlled. Furthermore, the lower monomer concentration or presence of nitrobenzene should have little effect upon the amount of grafted cellulose acetate.

The grafting reactions, when 57.5 and 60% styrene are used in the absence of nitrobenzene, follow the model for reaction-controlled growth. Trace additions of nitrobenzene at both of these monomer concentrations noticeably decrease the quantity of grafted polystyrene without appreciably affecting the percentage of grafted cellulose acetate. Since the reactions at these monomer concentrations are reaction-controlled in the absence of nitrobenzene, they should be reaction-controlled in the presence of nitrobenzene.

The chain propagation reactions at styrene concentrations of 65, 70, and 75% styrene are reaction-controlled in the presence of nitrobenzene. At any nitrobenzene concentration, an increase in the monomer concentration causes an increase in the amount of grafted polystyrene, unlike the trends found in the

diffusion-controlled cases. Substrate swelling apparently has little significance when conditions are reaction-controlled.

#### MOLECULAR WEIGHTS OF THE GRAFTED CHAINS

Table V lists the composition of the isolated graft polymer, expressed as the weight ratio of polystyrene to cellulose acetate, the number average molecular weight of the polystyrene side chains, and the number average molecular weight of some homopolystyrene samples formed in the bulk styrene solution surrounding the film. The styrene - pyridine ratio and the nitrobenzene concentration are also given in Table V.

The lack of reproducibility is again evident. The experimental scatter permits observation of only gross trends.

The most important observation found in Table V is the comparison between the molecular weight of the grafted side chains and that of the polystyrene produced in solution. These differences have been found in previous work, and are reviewed on page 14. They clearly indicate that the termination reaction occurring within the substrate is diffusion-controlled.

The molecular weight of the grafted side chains is higher than that of the solution-produced homopolymer despite two kinetic factors tending to reduce the side-chain molecular weight. First, because of the sensitivity of cellulose acetate toward radiation, the concentration of radicals within the substrate is relatively high compared to the radical concentration in the surrounding solution. Therefore, the rate of initiation within the film is higher than in the surrounding solution. Also, the monomer concentration within the film is relatively low, if only because a fraction of the total volume is occupied by the substrate. The lower monomer concentration and higher rate of radical production within the film

TABLE V

## NUMBER AVERAGE MOLECULAR WEIGHTS

Mole Ratio Styrene - Pyridine	Nitro- benzene, %	Weight Ratio Polystyrene/ Cellulose Acetate	Molecular Weights Grafted Side Chains	Molecular Weights Surrounding Solution
75/25	--	1.347	101,000 <sup>a</sup>	--
75/25	0.1	1.245	80,700	--
75/25	0.5	0.686	47,600	--
70/30 (A)	--	1.469	72,800 <sup>a</sup>	--
70/30 (B)	--	1.601	52,000 <sup>a</sup>	--
70/30 (A)	0.1	1.241	81,500	25,600
70/30 (B)	0.1	1.119	61,300	24,800
70/30 (A)	0.5	0.678	39,100	17,600
70/30 (B)	0.5	0.681	41,400	17,900
65/35 (A)	--	1.428	88,000 <sup>a</sup>	--
65/35 (B)	--	1.601	--	--
65/35 (A)	--	1.528	89,000 <sup>a</sup>	36,300
65/35 (B)	--	2.099	91,300 <sup>a</sup>	35,700
65/35 (A)	0.02	1.640	102,000	--
65/35 (B)	0.02	1.585	151,000	--
65/35 (A)	0.05	1.385	75,000	--
65/35 (B)	0.05	1.322	97,000	--
65/35 (A)	0.1	0.966	66,600	--
65/35 (B)	0.1	0.920	63,600	--
65/35 (A)	0.5	0.644	58,600	--
65/35 (B)	0.5	0.680	51,200	--
60/40 (A)	--	1.767	90,200 <sup>a</sup>	34,800
60/40 (B)	--	1.446	110,000 <sup>a</sup>	31,000
60/40 (A)	--	1.555	121,000 <sup>a</sup>	--
60/40 (B)	--	1.696	141,000 <sup>a</sup>	--
60/40 (A)	0.02	1.005	--	--
60/40 (B)	0.02	0.809	51,300	--
60/40 (A)	0.05	0.906	59,500	--
60/40 (B)	0.05	0.676	58,300	--
60/40	0.1	0.853	62,800	--
60/40	0.1	0.867	66,200	24,600
60/40 (A)	0.5	0.671	54,600	16,800
60/40 (B)	0.5	0.379	40,000	--
57.5/42.5	--	1.185	84,500 <sup>a</sup>	--
57.5/42.5 (A)	0.02	0.546	46,100	--
57.5/42.5 (B)	0.02	0.628	40,000	--
57.5/42.5 (A)	0.05	0.498	43,900	--
57.5/42.5 (B)	0.05	0.447	40,000	--

<sup>a</sup>Samples contained insoluble material. Molecular weights obtained on soluble portion.

tend to reduce the molecular weight of the polymer formed within the substrate. However, the observed higher molecular weights of the grafted side chains clearly illustrate the magnitude of the hindered termination rate.

All samples polymerized in the absence of nitrobenzene contained appreciable quantities of toluene-insoluble material, and only the molecular weights of the soluble portions are listed. Necessarily, any comparison between these values and the molecular weights of the polystyrene formed in the presence of nitrobenzene must be done with considerable reserve.

The other observable trends are the effects of increasing nitrobenzene concentration on the side-chain molecular weight at a given styrene concentration. These trends are shown in Fig. 6. At 75, 70, and 65% styrene, the side-chain molecular weights decrease from relatively high values with increasing nitrobenzene concentration. At 60 and 57.5% styrene concentrations, where substrate swelling is great, little change is seen with increasing nitrobenzene concentration.

It was shown on pages 40 and 41 that chain propagation is apparently reaction-controlled, and chain termination is diffusion-controlled in every styrene solution in the presence of nitrobenzene. At the higher styrene concentrations, the substrate interior is less swollen, and the probability of termination by macromolecular radical interaction is less likely under relatively nonswollen conditions. When macromolecular radical interaction is less probable, a relatively larger number of chains must be made incapable of further monomer addition. Since nitrobenzene adds to chain radicals and prevents further monomer addition to the chain end, relatively high percentages of nitrobenzene are needed to form low molecular weight side chains at the higher styrene concentrations. However, when the substrate is highly swollen in 60 and 57.5% styrene, interaction-

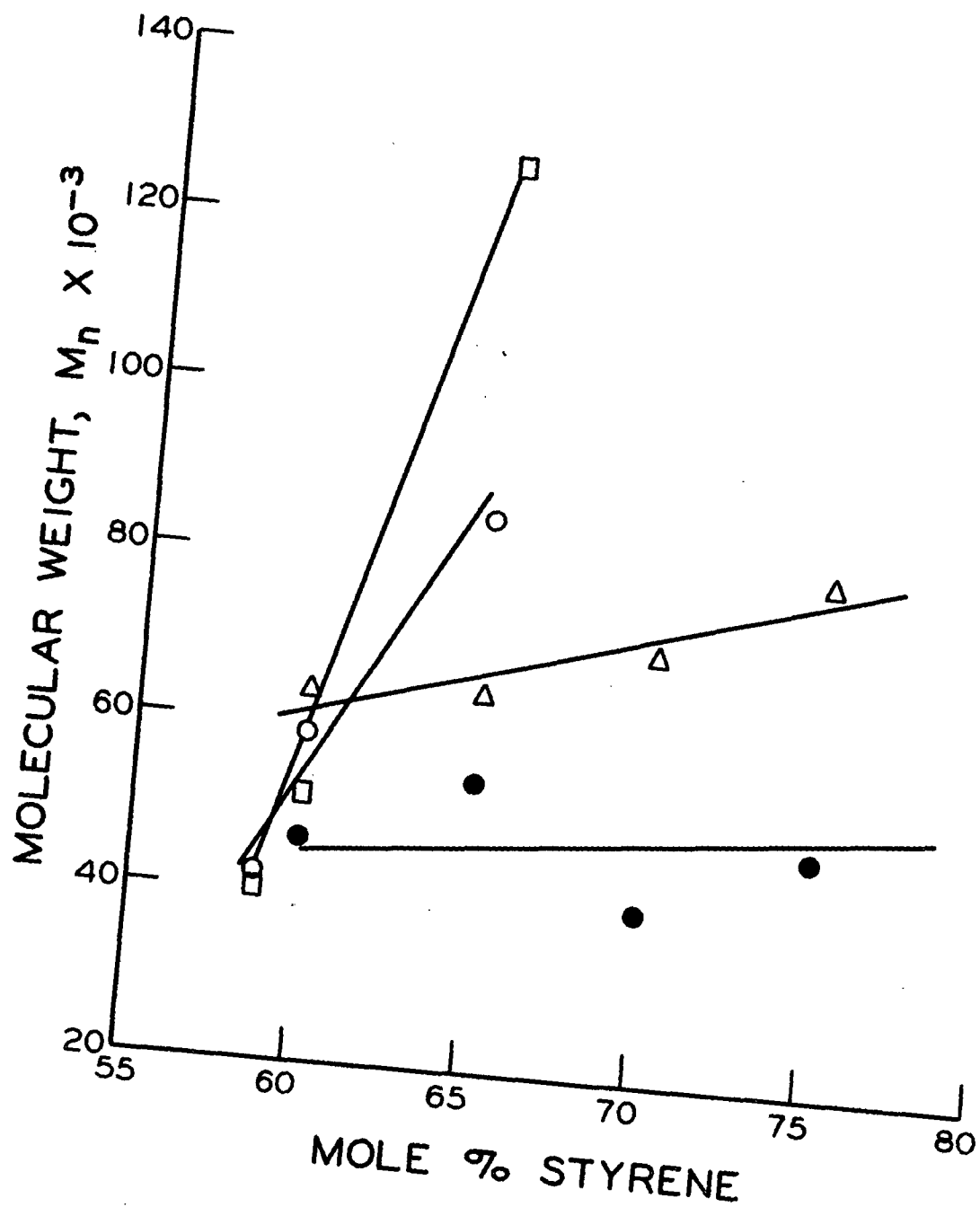


Figure 6. Number Average Molecular Weights of Polystyrene Side Chains;  $\square$  0.02% Nitrobenzene;  $\circ$  0.05% Nitrobenzene;  $\triangle$  0.10% Nitrobenzene;  $\bullet$  0.50% Nitrobenzene



of chain ends is more likely. Consequently, only trace additions of nitrobenzene are needed to form low molecular weight side chains.

# VISCOMETRY

Table VI presents the results of the intrinsic viscosity determinations. The extrapolated value of the intrinsic viscosity, together with the correlation coefficient of the slope and the corresponding number - average molecular weight, are shown as a function of the styrene - pyridine ratio and the nitrobenzene concentration. The correlation coefficients are generally acceptable, except for two samples. However, any correlation of the intrinsic viscosity values to the styrene - pyridine ratio or the nitrobenzene is usually quite uncertain. The intrinsic viscosity values appear to be badly scattered. Only the values corresponding to 65/35 styrene - pyridine solutions exhibit the expected downward trend with increasing nitrobenzene concentration.

TABLE VI  
INTRINSIC VISCOSITIES OF POLYSTYRENE SIDE CHAINS

Mole Ratio Styrene- Pyridine	Nitro- benzene, %	$[\eta]$ , dl./g.	Correlation Coefficient	$k_1$	Molecular Weight
65/35 (B)	0.02	0.727	0.998	1.125	151,000
65/35 (A)	0.05	0.640	0.998	0.585	97,000
65/35 (B)	0.05	0.573	0.995	0.620	75,000
65/35 (B)	0.10	0.529	0.984	0.275	63,600
65/35 (A)	0.50	0.553	0.999	0.938	58,600
60/40 (B)	0.02	0.487	0.999	0.620	51,300
60/40 (B)	0.02	0.507	0.985	0.535	51,300
60/40 (A)	0.05	0.585	0.944	0.370	59,500
60/40	0.10	0.435	0.996	0.873	66,200
60/40 (A)	0.50	0.279	0.966	0.519	54,600
57.5/42.5 (B)	0.02	0.495	0.959	0.373	40,000
57.5/42.5 (A)	0.05	0.207	0.603	--	43,000
57.5/42.5 (B)	0.05	0.321	-0.509	--	40,000

The Huggins' coefficient,  $k_1$ , is calculated from the slope of the curve of  $(\eta_{sp}/c)$  versus  $c$ . These values show no discernible trends, either with intrinsic viscosity values, the styrene - pyridine ratio or the nitrobenzene concentration. However, except for three samples, the Huggins' coefficients are greater than 0.5. These values are rather high, and suggest that the structure of the polystyrene is branched.

For a linear flexible polymer dissolved in a good solvent,  $k_1$  values of 0.30-0.40 are usually obtained (31). For example, the Huggins' coefficient for polystyrene in toluene is 0.38 (32). Branching or cross-linking results in a higher  $k_1$  value for these molecules than for linear molecules. The compact branched structure does not affect the solution viscosity as much as linear molecules at low solution concentrations (31). However, as the concentration increases, the denser branched molecules have a greater opportunity to interact, and the solution viscosity increases faster with concentration than corresponding increases with linear molecules.

Huggins' coefficient reflects the increase in solution viscosity with increasing solute concentration. In general, the viscosity of a dilute polymer solution increases more rapidly than the concentration (31). This behavior is due to increasing flow disturbances caused by a greater probability of interaction between macromolecules as the concentration increases (31).

Figure 7 shows a logarithmic plot of the intrinsic viscosity values as a function of the number average molecular weights. No correlation is apparent at styrene concentrations of 57.5 and 60%. However, at the highest styrene concentration, a satisfactory correlation is found.

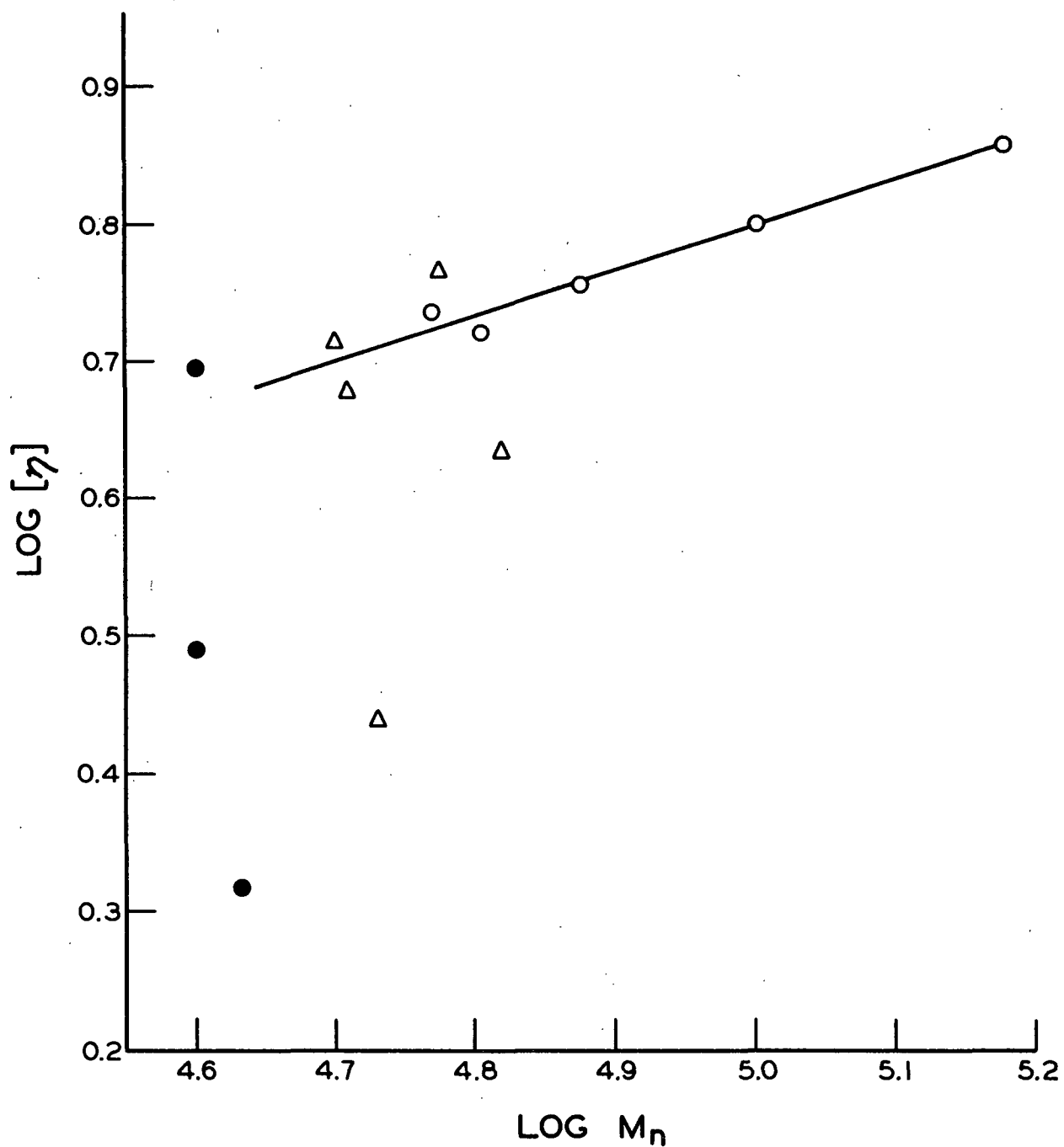


Figure 7.  $\log [\eta]$  vs.  $\log M_n$  for Polystyrene Side Chains;  
 ○ - 65-35 Styrene-Pyridine; Δ - 60-40 Styrene-Pyridine; ● - 57.5-42.5 Styrene-Pyridine

This satisfactory data can be treated by the empirical Mark-Houwink equation  
(31)

$$[\eta] = K M^a \quad (6).$$

From the slope of the line in Fig. 7, the exponent in the Mark-Houwink equation,  $a$ , is calculated to be 0.33. This value contrasts to the value of 0.73 found by Flory and Fox (32) for linear polystyrene in toluene.

The constant,  $a$ , is related to the configuration of the polymer molecule in solution, and can be predicted theoretically by assuming various models. The following is a listing of these models.

Model	$a$
Rigid Einstein sphere (34)	0
Nondraining tightly packed coil (23)	0.5
Free-draining loosely packed coil (23)	1.0
Rigid rod (35)	2.0

The calculated value of 0.33 indicates that these samples exhibit behavior intermediate between an Einstein sphere and a tightly packed coil. The exponent for linear polymers never falls below 0.5 (23). This compact structure suggests a branched molecule.

The scatter in the viscometric results is probably caused by a variable degree of branching of the polystyrene side chains. Another source of scatter is also apparent from the results of carbon-hydrogen-nitrogen analyses on two hydrolyzed graft polymer samples. The results of the analyses are as follows:

Mole Ratio Styrene - Pyridine	Nitro- benzene, %	C, %	H, %	N, %	O (by difference), %
70/30	--	91.49	7.85	0.83	--
70/30	0.1	89.96	7.97	0.83	1.24
100 (theoretical)		92.32	7.68	--	--

Both samples contain identical amounts of nitrogen, suggesting its source to be pyridine, and one sample contains oxygen, which presumably arises from incomplete hydrolysis of the cellulose acetate - polystyrene graft polymer. Residual carbohydrate fragments on the polystyrene chain could affect solvent-polymer interactions, and also cause error in the measured Huggins' coefficients and intrinsic viscosities.

#### CROSS-LINKING

All of the grafted polystyrene samples formed in the absence of nitrobenzene contained appreciable quantities of toluene-insoluble material. Yet every sample polymerized in the presence of nitrobenzene was completely toluene-soluble after acid hydrolysis. The insolubility of the samples polymerized without nitrobenzene was caused by either the presence of residual sugar units on these samples after hydrolysis, or cross-linking reactions which formed an insoluble gel. Attempts to devise means of completely dissolving the insoluble samples led to the conclusion that the insolubility was the result of polystyrene cross-linking reactions.

Direct evidence from the absence of residual carbohydrate material was obtained from the results of carbon-hydrogen-nitrogen analyses on two hydrolyzed graft polymer samples. These results have been presented before on this page. The toluene-soluble sample, which was polymerized in the presence of nitrobenzene, contains oxygen, presumably in the form of sugar residues. However, the insoluble sample contains no oxygen, and therefore has no carbohydrate fragments.

Other evidence for cross-linking was largely circumstantial. First, a number of known solvents for polystyrene did not completely dissolve the insoluble material. Benzene, toluene, dioxane, and dimethylformamide, all of which readily dissolve polystyrene, were used as solvents without success.

Secondly, presuming the insolubility to result from polar sugar residues remaining after hydrolysis, acetolysis of the insoluble polystyrene with acetic anhydride solutions containing equal volumes of either dimethylformamide, toluene, or dioxane was carried out at 60-70°C. for 24 hours. These reaction systems were designed to form a homogeneous system. Homopolystyrene dissolved in all three acetolysis systems; Whatman cellulose powder readily dissolved under the reaction conditions employed. However, the insoluble polystyrene was insoluble in all three acetolysis systems, and remained toluene-insoluble after these treatments. The lack of toluene-solubility after these treatments indicates that any residual carbohydrate fragments on the polymer had little effect on the solubility.

Also, a sample of the toluene-insoluble polystyrene was oxidized in aqueous periodic acid (approximately 0.5M) for 24 hours in the dark at room temperature. The sample remained insoluble in toluene.

The failures to obtain a toluene-soluble polystyrene, and the direct evidence for the absence of carbohydrate fragments, indicate that the insolubility of samples formed in the absence of nitrobenzene results from cross-linking reactions of polystyrene. Chapiro's text (8) thoroughly reviews the cross-linking of polystyrene by ionizing radiation, both in concentrated solution and in the solid state. The 20-megarad radiation dosage employed in this study is high enough to produce an insoluble cross-linked polystyrene network. Also Huang, Immergut, and Rapson (10) found some evidence for formation of an insoluble, cross-linked

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polystyrene gel in their study of the graft polymerization of styrene onto cellulose.

#### REASONS FOR CROSS-LINKING

Formation of a cross-linked network requires that any given polymer molecule have two or more radical sites for further chain growth or termination with other macromolecular radicals. Generation of radicals by radiolysis of polystyrene is quite probable. Polystyrene contains an aliphatic side group which is more sensitive to effects of gamma radiation than more resonance-stabilized species such as styrene or benzene (8). Evidence for initiation of additional radicals on polystyrene is obtained from the results of the viscometric measurements. These results, which were obtained on noncross-linked samples, indicated that some high molecular weight polystyrene samples were branched. Since a branched polystyrene must have had more than one radical site, multiradical polystyrene during irradiation can be inferred.

Coupling of multiradical polymers first forms a branched molecule from two linear polymers, and the resulting adduct still contains more than one radical site. As coupling reactions proceed, the degree of branching increases. Ultimately, an insoluble network is formed with the molecular weight approaching infinity.

The probability of cross-linking increases as the molecular weight of the polystyrene increases. A higher molecular weight makes formation of two or more radicals on a polystyrene chain more likely, and the probability of branching is therefore increased. The effect of the molecular weight upon the amount of cross-linked polystyrene is seen in Fig. 8. The amount of toluene-insoluble gel increases with increasing molecular weight of the associated soluble phase.

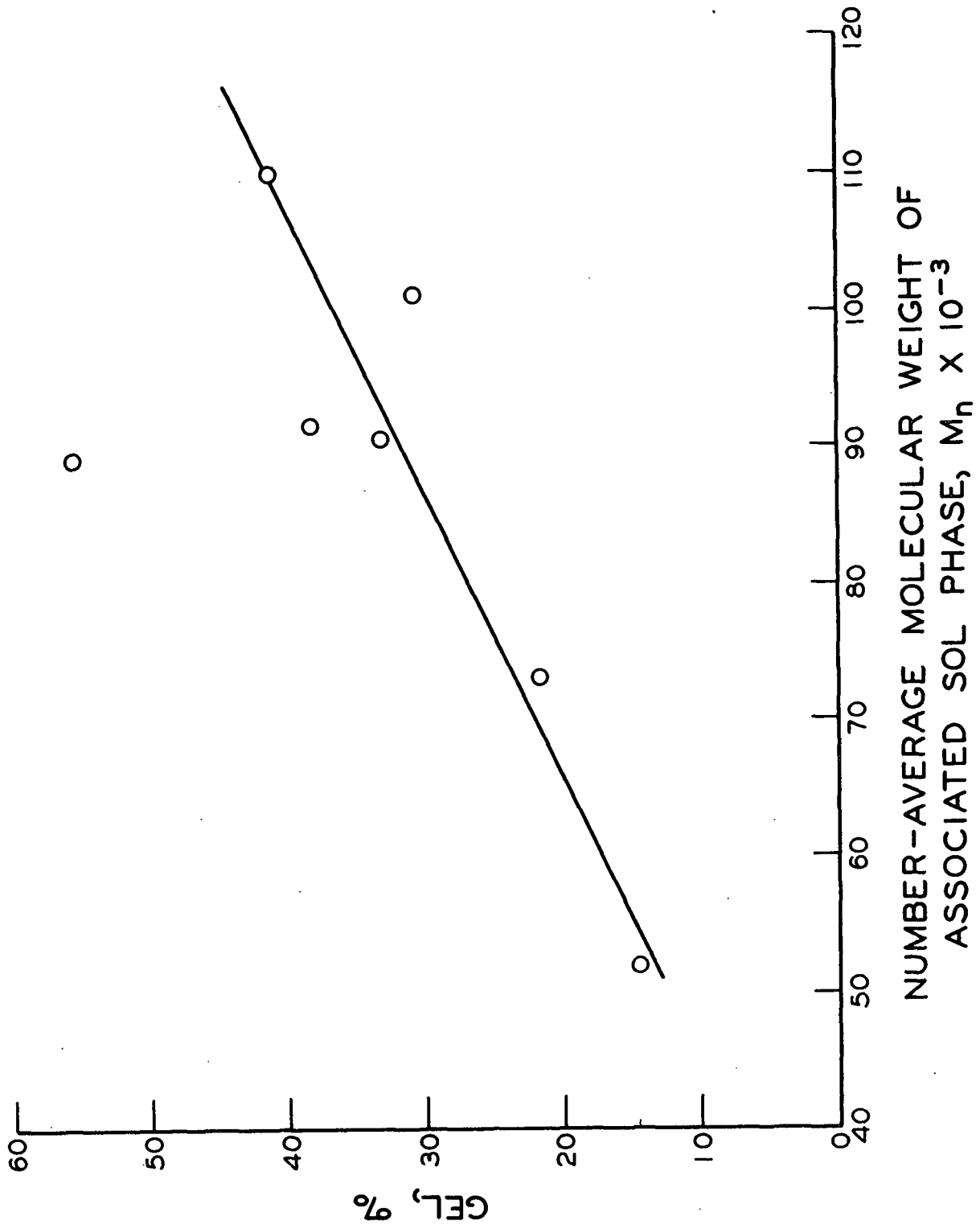


Figure 8. Amount of Cross-Linked Material



## ACTION OF NITROBENZENE

As illustrated on page 22, nitrobenzene reacts with polystyrene radicals to form an adduct which is too unreactive for further monomer addition. In terminating with another polystyrene radical, this nitrobenzene adduct radical disproportionates instead of coupling. In disproportionation, radicals terminate without an increase in the molecular weight. Consequently, cross-linking reactions with the subsequent gel network formation is highly improbable when nitrobenzene is present.

## FREQUENCY OF GRAFTING

Table VII shows the frequency of polystyrene grafting, which is the number of polystyrene chains per cellulose acetate molecule, as a function of the styrene - pyridine ratio, and the nitrobenzene concentration. The frequency of grafting was calculated from the weight ratio of polystyrene to cellulose acetate, divided by the ratio of the number average molecular weights of polystyrene and cellulose acetate, respectively. Also shown in Table VI is the reciprocal of the grafting frequency, expressed as the number of cellulose acetate molecules per polystyrene molecule.

In Table VII, it is seen that between 0.25 and 0.75 polystyrene chains per cellulose acetate chain are found. Usually, the values are between 0.3 and 0.4. Visible trends with reaction variables such as styrene - pyridine ratio, and the nitrobenzene concentration, are not obvious. The magnitude of the grafting frequencies is much lower than expected. A pure sample of graft polymer would be expected to have about one or more polystyrene molecules per molecule of cellulose acetate. The low grafting frequencies suggest that the graft polymer samples are impure and contain appreciable amounts of occluded cellulose acetate. If it is

TABLE VII  
FREQUENCY OF GRAFTING

Mole Ratio Styrene - Pyridine	Nitro- benzene, %	Weight Ratio Polystyrene/ Cellulose Acetate	Molecular Weights Grafted Side Chains	Molar Ratio <sup>a</sup> Polystyrene/ Cellulose Acetate	Molar Ratio <sup>a</sup> Cellulose Acetate/ Polystyrene
75/25	--	1.347	101,000	0.333	3.0
75/25	0.1	1.245	80,700	0.378	2.6
75/25	0.5	0.686	47,600	0.353	2.8
70/30 (A)	--	1.461	72,800	0.490	2.0
70/30 (B)	--	1.601	52,000	0.755	1.3
70/30 (A)	0.1	1.241	81,500	0.736	1.4
70/30 (B)	0.1	1.119	61,300	0.613	1.6
70/30 (A)	0.5	0.678	39,100	0.425	2.4
70/30 (B)	0.5	0.681	41,400	0.408	2.4
65/35 (A)	--	1.428	88,000	0.398	2.5
65/35 (B)	--	1.601	--	--	--
65/35 (A)	--	1.528	91,300	0.429	2.3
65/35 (B)	--	2.099	89,000	0.428	2.3
65/35 (A)	0.02	1.640	102,000	0.394	2.5
65/35 (B)	0.02	1.585	151,000	0.257	3.9
65/35 (A)	0.05	1.385	75,000	0.435	2.3
65/35 (B)	0.05	1.322	97,000	0.334	3.0
65/35 (A)	0.1	0.966	66,600	0.356	2.8
65/35 (B)	0.1	0.920	63,600	0.355	2.8
65/35 (A)	0.5	0.644	58,600	0.267	3.7
65/35 (B)	0.5	0.680	51,200	0.325	3.1
60/40 (A)	--	1.767	90,200	0.480	2.1
60/40 (B)	--	1.446	110,000	0.322	3.1
60/40 (A)	--	1.555	121,000	0.314	3.2
60/40 (B)	--	1.696	141,000	0.294	3.4
60/40 (A)	0.02	1.005	--	--	--
60/40 (B)	0.02	0.809	51,300	0.386	2.6
60/40 (A)	0.05	0.906	59,500	0.341	2.9
60/40 (B)	0.05	0.676	58,300	0.284	3.5
60/40	0.1	0.853	62,800	0.339	2.9
60/40	0.1	0.867	66,200	0.278	3.6
60/40 (A)	0.5	0.671	54,600	0.302	3.3
60/40 (B)	0.5	0.379	40,000	0.232	4.3
57.5/42.5	--	1.185	84,500	0.343	2.9
57.5/42.5 (A)	0.02	0.546	46,100	0.290	3.4
57.5/42.5 (B)	0.02	0.628	40,000	0.374	2.7
57.5/42.5 (A)	0.05	0.498	43,900	0.278	3.6
57.5/42.5 (B)	0.05	0.447	40,000	0.329	3.0

<sup>a</sup> Molecular weight of cellulose acetate in dimethylformamide is 24,500.

assumed that the pure graft polymer contained one polystyrene molecule per cellulose acetate molecule, then the amount of occluded unreacted cellulose acetate usually would exceed the amount of grafted cellulose acetate.

## CONCLUSIONS

Styrene was grafted from pyridine solution onto swollen cellulose acetate film by direct irradiation from  $\text{Co}^{60}$  gamma rays at a dose rate of  $0.44 \times 10^6$  rads per hour for a total dose of  $20 \times 10^6$  rads. Known small amounts of nitrobenzene were added to most of the styrene - pyridine solutions.

The following conclusions are based upon the amounts of grafted polystyrene and grafted cellulose acetate. In the absence of nitrobenzene, graft polymerization was limited by diffusion-controlled growth processes when styrene concentrations were 65, 70, 75 mole % styrene. At styrene concentrations of 57.5 and 60%, when the substrate is highly swollen, the monomer transport rate is sufficiently rapid so that chain growth is reaction-controlled. In the presence of nitrobenzene, chain propagation is reaction-controlled at all styrene concentrations.

Number-average molecular weights of the polystyrene side chains, measured after removal of the cellulose backbone, were always higher than those of the corresponding homopolymers formed in solution. This observation indicates that chain termination is diffusion-controlled within the swollen film. Nitrobenzene additions reduced the molecular weight. However, the amount of nitrobenzene necessary for significant molecular weight reduction was apparently dependent upon the state of substrate swelling. At the lower degree of substrate swelling, relatively large amounts of nitrobenzene were necessary for significant D.P. reduction. When the substrate was highly swollen, trace additions of nitrobenzene caused marked reductions in the D.P., while further additions had little effect.

Appreciable insoluble residues in the polystyrene formed in the absence of nitrobenzene is strong circumstantial evidence that the polymer contained appreciable fractions of cross-linked gels. The amount of insoluble material increased with increasing molecular weight of the associated soluble polystyrene. The cross-linking is believed to originate from coupling reactions between branched units on the grafted polystyrene chain. These branched polystyrene chains were initiated by radicals formed on the grafted side chain. Experimental evidence for branched polystyrene was obtained from the results of intrinsic viscosity measurements, which indicate that the polystyrene was branched.

Nitrobenzene prevented the formation of cross-linked gels in all cases. This compound adds to chain radicals, forming an adduct too unreactive for further addition. Termination between this nitrobenzene adduct radical and the polystyrene radical chain end proceeds by disproportionation, and not by coupling of chain ends. Therefore, the probability of cross-linking in the presence of nitrobenzene is greatly diminished.

The number of polystyrene side chains per cellulose acetate chain was determined, and found to exhibit no observable trends with either the styrene - pyridine ratio or with the nitrobenzene concentration. The magnitude of the values suggested that between two to four cellulose acetate chains were connected to one polystyrene chain, and suggest that the samples contain occluded ungrafted cellulose acetate that was not removed in the purification procedure.

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# APPENDIX I

## KINETICS OF HOMOGENEOUS FREE RADICAL POLYMERIZATION

Free radical addition polymerization proceeds by a classical chain reaction involving initiation, propagation, and termination. In radiation polymerization, the initiation step is brought about by the absorption of radiation energy. The secondary ionization and/or excitation processes lead to the production of free radicals. In the propagation step, a free radical adds onto a double bond of a monomer molecule, thereby generating another free radical. This process continues until the activity of the growing polymer is destroyed. In homogeneous free radical polymerization, chain termination occurs almost exclusively by mutual interaction of two radicals. These elementary steps can be written schematically as follows:

<u>Process</u>	<u>Rates</u>
Initiation	
$A \rightarrow 2 R\cdot$	$R_1 \quad (1)$
Propagation	
$R\cdot + M \rightarrow RM\cdot$	
$RM_n\cdot + M \rightarrow RM_{n+1}\cdot$	$k_p [RM\cdot] [M] \quad (2)$
Termination	
$RM_n\cdot + RM_m\cdot \rightarrow D_{n+m}$	$k_t [RM\cdot]^2 \quad (3)$

Here A is any molecule present in the reaction mixture, R· is a primary radical, M the monomer, RM· a growing polymer chain, and D is a "dead" polymer.

Another elementary step of importance is the chain transfer reaction:



The rate constants for propagation, termination, and chain transfer, which are  $k_p$ ,  $k_t$ , and  $k_{tr}$ , respectively, are assumed to be independent of chain length. This assumption is generally valid for reactions in homogeneous solution. The polymer molecule is considered as a loosely coiled chain in which the growing end has considerable freedom of movement. Its reaction properties are influenced only by the immediately adjacent monomer units. A more detailed discussion of the reactivity of macromolecules is found in Flory (23).

If the rates of formation and destruction of free radicals are equal (i.e., the "steady-state assumption"):

$$R_i = 2 k_t [RM\cdot]^2 \quad (5).$$

The basis for the steady-state assumption is comprehensively discussed in Walling (35a). The stationary state concentration of radicals is:

$$[RM\cdot] = (R_i/2k_t)^{1/2} \quad (6).$$

The consumption of monomer is practically limited to the propagation step, so that the overall reaction rate,  $R$ , is

$$R = k_p [RM\cdot] [M] = [k_p R_i^{1/2} / (2k_t)^{1/2}] [M] \quad (7).$$

This is the classical kinetic equation which shows that the reaction rate is proportional to the square root of the rate of initiation.

The degree of polymerization is the number of monomer units divided by the number of molecules. If termination occurs exclusively by combination of chain ends:

$$P_N = R_p / R_t = \frac{k_p [M]}{(2k_t)^{1/2} R_i^{1/2}} \quad (8).$$

With the monomer of interest in this study, styrene, results presented by Chapiro (8) confirm the validity of Equation (8).

#### DILUTION EFFECTS

The effects of added substances in the radiation polymerization of vinyl monomers is an important consideration. In radiation polymerization, the addition of an "inert" solvent is impossible. Any added solvent leads to the production of free radicals, which, in turn, contributes to chain initiation.

However, further complications may arise in the radiolysis of binary mixtures. In a mixture of A and B, it is often found that the rate of radical production of A is modified by the presence of B. For example, the energy absorbed by compound A can be transferred to B, which is disrupted in the process. Such "energy transfer processes" lead to complicated kinetic relationships between the rate of formation of free radicals and the chemical composition of the mixture.

In the absence of energy transfer effects, the rate of initiation of a monomer-solvent mixture is:

$$R_i = I (\phi_M[M] + \phi_S[S]) \quad (9)$$

where  $\phi_M[M]$  and  $\phi_S[S]$  are the rates of free radical production in the monomer and solvent, respectively, expressed as moles per liter per unit radiation dose, and  $I$  is the dose rate. Substitution into Equation (7) yields the expression for the overall reaction rate  $R$ .

$$R = \frac{k_p}{k_t} (\phi_M I)^{1/2} [M]^{3/2} \left( 1 + \frac{\phi_S[S]}{\phi_M[M]} \right)^{1/2} \quad (10).$$

It is more concise to express the relation for the reaction rate as a ratio of the rate of polymerization of bulk monomer,  $\underline{R}_O$ .

$$R_O = (k_p/k_t^{1/2})(\phi_M I)^{1/2} [M_O]^{3/2} \quad (11).$$

Furthermore, after expressing concentrations in terms of mole fractions,  $\underline{m}$ , and, accounting for the molar volumes  $\underline{v}_m$  and  $\underline{v}_s$  of monomer and solvent, respectively, the following relationship is obtained:

$$\frac{R}{R_O} = \left[ \frac{1}{m + (1-m)(v_s/v_m)} \right]^{3/2} \left[ 1 + \frac{\phi_s}{\phi_m} \cdot \frac{(1-m)}{m} \right]^{1/2} m^{3/2} \quad (12).$$

The first term is close to unity and is essentially unaffected by concentration changes. A second constant,  $(\phi_s/\phi_m)$ , can be made into a relative ratio  $(\phi_{rel})$ . Figure 9 illustrates Equation (12), in which  $R/R_O$  and  $\underline{m}$  are correlated and  $\phi_{rel}$  is plotted as a parameter.

In the absence of chain transfer reactions, the degree of polymerization is:

$$P_N = (k_p/k_t^{1/2})(\phi_M I)^{-1/2} [M]^{1/2} (1 + \phi_{rel}([S]/[M]))^{-1/2} \quad (13).$$

Experimental verification of the "simple dilution effect" is relatively uncommon. Some examples include styrene in toluene and in some halogenated compounds.

#### ENERGY TRANSFER PROCESSES

When a mixture of two components,  $\underline{A}$  and  $\underline{B}$ , is subjected to ionizing radiation, two types of excited species,  $\underline{A}^*$  and  $\underline{B}^*$ , are formed in the primary act. Each of these may react with homolytic bond scission. Alternatively, each may react with an unexcited neighbor and transfer its energy to the latter. In such an event, the overall rate of radical production is not only dependent upon the component

concentration and the relative lability of each component to radiolysis, but also on the probabilities of various energy transfer steps.

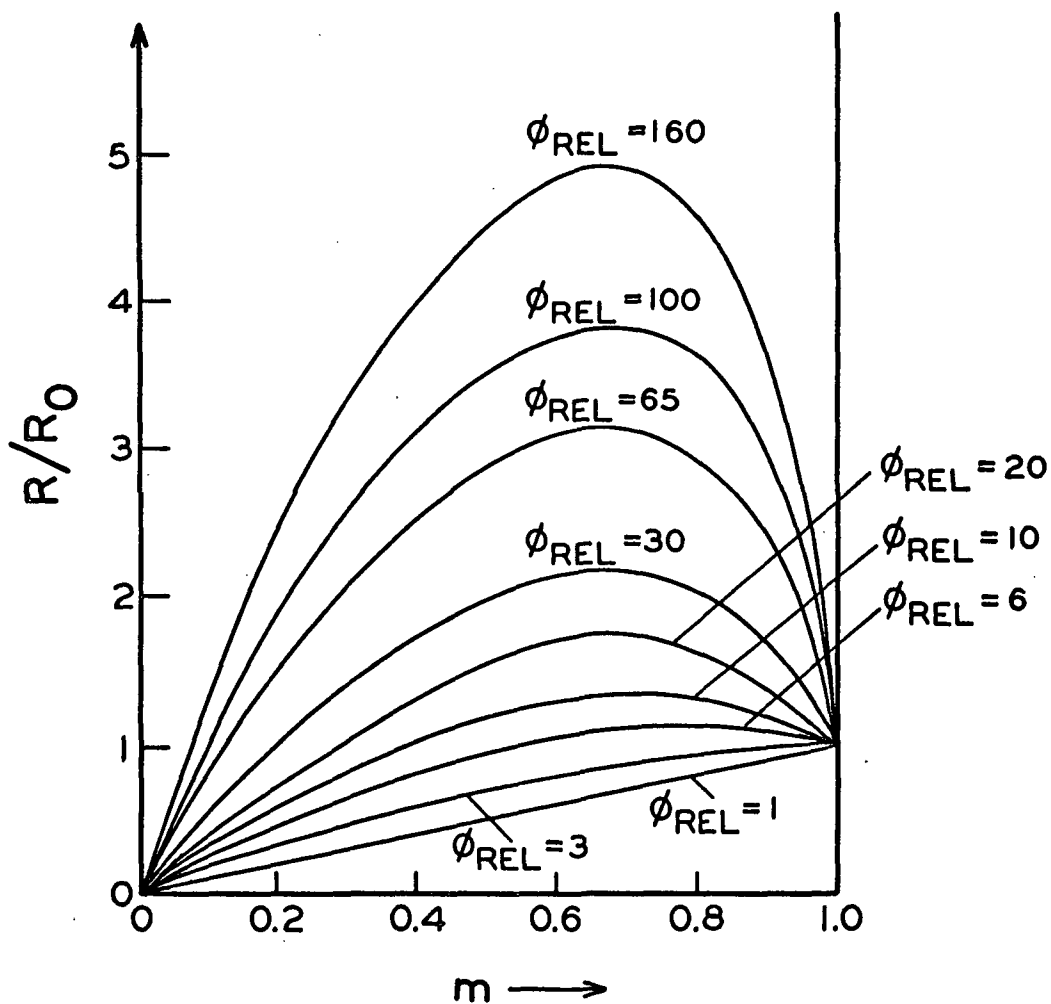
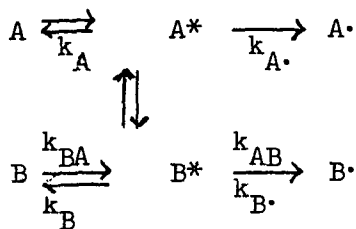


Figure 9. Theoretical Plot of the Relative Rates of Polymerization [From Chapiro (8, Chap. 7, p. 252)]

Kinetic analysis of energy is complicated, but revealing. The processes are:



It is considered that A and B are activated to A\* and B\*, respectively. These transient species can either:

1. Deactivate by collision with other molecules,  $k_{\underline{A}}$  and  $k_{\underline{B}}$ ,
  2. Disrupt into free radicals,  $k_{\underline{A}\cdot}$  and  $k_{\underline{B}\cdot}$ , or
  3. Transfer their excitation to the partner component,  $k_{\underline{AB}}$  and  $k_{\underline{BA}}$
- ( $k_{\underline{AB}}$  refers to energy transfer from A to B).

Let

$$\phi_{\text{rel}} = \frac{B}{A} = \frac{k_{\underline{B}\cdot} / (k_{\underline{B}} + k_{\underline{B}\cdot})}{k_{\underline{A}\cdot} / (k_{\underline{A}} + k_{\underline{A}\cdot})} \quad (14),$$

$$P_{\underline{AB}} = k_{\underline{AB}} / (k_{\underline{A}} + k_{\underline{A}\cdot}) \quad (15),$$

$$P_{\underline{BA}} = k_{\underline{BA}} / (k_{\underline{B}} + k_{\underline{B}\cdot}) \quad (16).$$

Equation (14) is the ratio of the probability of formation of free radical B from excited B\* in the radiolysis of pure B to the corresponding probability for pure compound A. Equations (15) and (16) are the probabilities of energy transfer from A\* to B and from B\* to A, respectively, with respect to the sum of the probabilities of collisional deactivation and homolytic disruption of the excited states. A lengthy derivation, found in Chapiro (8), leads to the following expression for the overall polymerization rate in solution,  $R$ , as a function of the rate in pure monomer,  $R_0$ . This expression is in terms of the mole fraction of monomer,  $m$ .

$$\frac{R}{R_0} = m \left[ \frac{1}{m + (1-m)(v_s/v_m)} \right]^{3/2} \left[ \frac{1 + \phi_{\text{rel}} P_{\text{rel}} (1-m)/m}{1 + P_{\text{rel}} (1-m)/m} \right]^{1/2} \quad (17).$$

Energy transfer effects are quite important when considering the polymerization of aromatic vinyl monomers such as styrene. The benzene ring is stabilized by resonance and any activated state may be likely to lose its energy through internal conversion.

## APPENDIX II

### DIFFUSION-CONTROLLED TERMINATION

Because of the ease of radical combination, the chain termination reaction is likely to be diffusion-controlled. The effects of diffusion-controlled termination are frequently found at high percentage monomer conversions, and with polymerization reactions in a solvent which precipitates the polymer. With the homogeneous bulk polymerization of acrylic monomers (36-38), vinyl acetate (39) and, to some extent, styrene (40), the conversion-time curves follow a pattern typical of autocatalytic reactions. The polymerization first proceeds at a constant rate until a critical conversion is reached. At this point, the rate suddenly accelerates to a high value. Simultaneously, an increase in the molecular weight of the polymer is found. Furthermore, the heat of polymerization is not readily dissipated in the resulting viscous medium. Because these effects usually occur when the reaction mixture is very viscous, the process is referred to as the "Trommsdorff effect" or the "gel effect."

Considerable evidence indicates that the above-mentioned effects are caused by a diffusion-controlled termination. Benson and North (41) studied the effect of viscosity upon the absolute rate constants for the polymerization of methyl methacrylate and butyl acrylate. In varying the viscosity over a thousandfold range, they found that the propagation rate constant,  $k_p$ , was unaffected by the viscosity of the medium. However, the termination rate constant,  $k_t$ , decreased considerably with increasing viscosity. North and Reed (42) considered that the diffusion occurs in two stages. The first is the translational diffusion of the center of gravities of the two macromolecular radicals. The second stage is the segmental diffusion of the radical chain ends to form a collision pair. By means of radioactive tracer techniques, they concluded that diffusion of chain segments

was the rate-controlling termination step in the polymerization of methyl methacrylate.

The decrease in the termination rate constant has serious kinetic consequences. The lifetime of the chains is considerably increased, and after-effects are likely to arise. The decrease in the rate of termination is not compensated with a corresponding decrease in the rate of initiation. An unsteady-state situation arises that makes steady-state kinetics inapplicable. Also, the termination rate constant is a function of chain length and polymer configuration in solution. Consequently, rigorous kinetic treatment of this phenomena is difficult, if not impossible.